VOL. XVII. [JULY, 1895.] No. 7.

AMERICAN CHEMICAL JOURNAL.

SOME NOTES ON MOLECULAR AND ATOMIC REFRACTION.

BY W. F. EDWARDS.

In a paper[1] read at the Brooklyn meeting of the American Association for the Advancement of Science, I offered a new formula, $\frac{P(M-1)}{MD}$, for molecular refraction, and gave examples to show that the formula was sufficiently concordant with experiment to warrant further investigation. It was also shown that in the cases of five alcohols, five aldehydes, six acids, and seven ethereal salts, the numbers representing the difference of molecular refraction for a difference of CH_2 in the molecular formula were in favor of the formula $\frac{P(M-1)}{MD}$ when compared with the formula $\frac{P(M^2-1)}{(M^2+2)D}$ the difference between the extreme values being 1.70 per cent. of the mean value in the case of the former, and 2.82 per cent. of the mean value in the case of the latter.

In this paper a number of examples were given to show that the difference in the molecular refraction for a difference of CH_2 in the molecular formula was greater when an acid was compared with an ethereal salt, than when a series of like

[1] This JOURNAL, **16**, 625.

compounds, such as alcohols, aldehydes, acids, etc., were compared. In the present paper this comparison is extended to twenty-one cases of acids and ethereal salts and confirms the result obtained before for the formula $\frac{P(M-1)}{MD}$, but gives a doubtful result as regards the Lorentz-Lorenz formula.

The chief purpose of the present paper is to give a somewhat extended comparison of the three formulæ, $\frac{P(M-1)}{D}$, $\frac{P(M^2-1)}{(M^2+2)D}$, and $\frac{P(M-1)}{MD}$, and to determine numbers for the atomic refractions of carbon, hydrogen, oxygen, nitrogen, chlorine, bromine, iodine, and sulphur, for the last formula, more especial attention being given to the determination of numbers for the first four elements mentioned.

In table I which follows—divisions *A* (hydrocarbons), *B* (alcohols), *C* (aldehydes), *D* (acids), *E* (ethereal salts), *F* (nitrogen compounds), and *G* (sulphur compounds)—the indices of refraction are given for sodium light. The molecular refractions and differences for CH_2 are, therefore, for sodium light.

Several considerations have led me to give these numbers for sodium light. Among them may be mentioned: (1) the ease with which sodium light can be obtained in any laboratory; (2) sodium light can be used with any refractometer; (3) some instruments, like that after Abbé, have a compensating device by the use of which sunlight may be used for obtaining the indices of refraction for sodium light; (4) the indices of refraction of gases are more generally given for sodium light; (5) many laboratories have polariscopes of the Laurent type, and with it some contrivance for obtaining a suitable sodium light. It seems to me that if we have numbers for sodium light there will be a more general comparison possible and a more general determination of molecular refraction for the reasons before stated.

As an example of greater possibility of comparison may be cited the hydrocarbons from octane to hexadecane in division *A* of table I. So far as I know the indices of refraction of these hydrocarbons have not been given for any other than

sodium light as found in the paper of Bartoli and Stracciati.[1] These investigators obtained their hydrocarbons by painstaking fractionation of American petroleum, and, while the portions used distilled at an approximately constant temperature, they cannot, of course, be considered as pure. It will be noticed, indeed, that the temperature of ebullition was about 10° below that given for corresponding hydrocarbons by Krafft.[2]

It is much to be regretted that Krafft did not supplement his excellent work by a more extended determination of the physical properties. It is also to be regretted that Bartoli and Stracciati, after finding the temperature of ebullition, do not state the pressure, and, after finding the density at 0° C. and the coefficients α and β of the formula $D_t = D_0 (1 - \alpha t - \beta t^2)$; the coefficients of expansion between 0° and 30° C. and between 0° and the temperature of ebullition; the molecular volume at the temperature of ebullition; the specific heat; the constants of capillary action; the electrical properties; and the indices of refraction for sodium light, did not determine the indices of refraction for at least light of one other color so that some idea of the dispersive power of the substances could be obtained. The day has gone by when the chemist can ignore the physical properties of the substances with which he works. It may be said, also, that the physicist cannot ignore the chemical constitutions of the substances with which he works. The ultimate aims of the physicist and the chemist are, alike, the determination, as nearly as may be, of the very nature of matter itself. If the chemist has not the means of determining the physical constants of new compounds—or old ones, for that matter—his compound should be turned over to the physicist who should be glad of an opportunity to add to the record of physical constants. The chemist should be held by a similar bond to aid the physicist. This co-operative way of working would leave no excuse for the omission of the physical properties of a substance whether the discoverer be a chemist or a physicist.

[1] Ann. chim. phys., [6] **7**, 375-383 (1886).

[2] Ber. d. chem. Ges., **15**, 1687, 1711.

The headings of the column in table I are, in general, a sufficient explanation of the numbers in those columns. Perhaps, however, it is desirable to call attention to the columns headed "difference for CH_2," for the purpose of explaining the cases where there are two differences given. In division *E* we have ethyl acetate with differences 6.81 and 6.96, in the first column headed "differences for CH_2." In this case the number for ethyl acetate has been compared with that of methyl acetate and that of ethyl formate. The same explanation applies to the second and third columns headed "difference for CH_2." In divisions *H*, *I*, *J*, and *K*, *M* is given for red hydrogen light.

In calculating the number for molecular refraction, wherever the specific gravity or index of refraction has been given to the fifth decimal, the fifth decimal has been omitted if less than 5, and where 5 or more than 5, 1 has been added to the fourth decimal figure. The specific refraction has been determined to the fourth decimal place before multiplying by the molecular weight. The third decimal of the molecular refraction has been omitted when under 5; when 5 or more, 1 has been added to the second decimal figure.

Where *M* is calculated it is by means of Cauchy's dispersion-formula as given in Landolt and Börnstein's *Tabellen*.

If we consider x as the greatest error in the numbers representing molecular refraction, the number for pentane, division *A*, first column headed molecular refraction, would be $41.26 \pm x$ and for hexadecane it would be $126.33 \pm x$. Assume that it is $-x$ in the first case and $+x$ in the second case, then the difference for CH_2 is $(126.33 + x) - (41.26 - x)$ divided by eleven, the number of times CH_2 must be added to the pentane molecule to make the hexadecane molecule. This gives an average difference from pentane to hexadecane of $7.73 + 2/11\ x$ and is correct to within some quantity not greater than $\frac{2x}{11}$. The differences for CH_2 in division *A* show that each CH_2 added to the pentane molecule adds an approximately equal increment to the numbers standing for the molecular refraction. If the number found in this way be averaged with the mean difference of division *A*, we have:

$$7.73 + 7.76 \div 2 = 7.74.$$

TABLE I.

Substance.	Formula.	Mol. weight.	Temperature.	Spec. grav. at $t°/4°$.	Index of refraction for ray D.	Molecular refraction $\frac{P(M-1)}{D}$.	Difference for CH_2.	Molecular refraction. $\frac{P(M^2-1)}{(M^2+2)D}$	Difference for CH_2.	Molecular refraction. $\frac{P(M-1)}{ND}$.	Difference for CH_2.	From the data of	Remarks.
A: Hydrocarbons.													
Isopentane	C_5H_{12}	72.0	6.5°	0.6365	1.3649	41.26		25.27		30.24		Gladstone.	
" (?)	"	"	16.	0.6174	1.35830	41.76		25.85		30.74		Bartoli and Stracciati.	B. P. 30°.
Hexane	C_6H_{14}	86.0	16.	0.6765	1.38547	49.11	7.85	29.84	4.57	35.36	5.12	" " "	" 68°.
"	"	"	25.5	0.6317	1.3602	49.03	7.77	30.01	4.16	36.04	5.80	Gladstone.	" 48°–52°.
Heptane	C_7H_{16}	100.0	16.	0.7144	1.40307	56.04	6.93	34.20	4.36	40.25	4.89	Bartoli and Stracciati.	" 92°–94°.
"	"	"	7.6	0.6935	1.3945	59.90	7.87	34.53	4.69	40.79	5.43	Gladstone.	
"	"	"	12.	0.6895	1.3917	56.81	7.78	34.53	4.67	40.82	5.46	"	
"	"	"	23.	0.6869	1.3867	56.89	7.86	34.55	4.71	40.95	5.59	"	
Octane	C_8H_{18}	114.0	16.	0.7299	1.41202	64.40	8.36	38.92	4.72	45.62	5.37	Bartoli and Stracciati.	B. P. 116°–118°.
Nonane	C_9H_{20}	128.0	"	0.7457	1.42073	72.19	7.79	43.39	4.37	50.82	5.20	" " "	" 136°–138°.
Decane	$C_{10}H_{22}$	142.0	"	0.7501	1.42574	79.95	7.76	48.08	4.69	56.07	5.25	" " "	" 158°–162°.
Undecane	$C_{11}H_{24}$	156.0	"	0.7673	1.43136	87.67	7.72	52.62	4.54	61.27	5.20	" " "	" 180°–182°.
Dodecane	$C_{12}H_{26}$	170.0	"	0.7769	1.43676	95.54	7.87	57.29	4.67	66.52	5.25	" " "	" 198°–200°.
Tridecane	$C_{13}H_{28}$	184.0	"	0.7861	1.44227	103.22	7.68	61.81	4.52	71.95	5.43	" " "	" 218°–220°.
Tetradecane	$C_{14}H_{30}$	198.0	"	0.7948	1.44809	111.67	8.45	66.71	4.90	77.08	5.13	" " "	" 236°–240°.
Pentadecane	$C_{15}H_{32}$	212.0	"	0.8096	1.45319	118.51	6.84	70.79	4.08	81.86	4.78	" " "	" 258°–262°.
Hexadecane	$C_{16}H_{34}$	226.0	"	0.8167	1.45697	126.33	7.82	75.37	4.58	86.78	4.92	" " "	" 278°–282°.
						Mean..	7.76		4.56		5.26		
Benzene	C_6H_6	78.0	10.	0.8903	1.5078	44.48		26.11		29.50		Gladstone.	
"	"	"	20.	0.8799	1.5014	44.44		26.14		29.60		Brühl.	
Toluene	C_7H_8	92.0	7.5	0.8704	1.4982	52.76	8.28	30.99	4.88	35.22	5.72	Gladstone.	
"	"	"	20.	0.8656	1.4955	52.66	8.22	31.05	4.91	35.21	5.61	Brühl.	
o-Xylene	C_8H_{10}	106.0	18.	0.8632	1.4966	60.98	8.22	35.90	4.91	40.75	5.53	Gladstone.	
m-Xylene	"	"	15.5	0.8726	1.5020	60.98	8.22	35.85	4.86	40.60	5.38	"	
p-Xylene	"	"	16.	0.8488	1.4846	60.52	7.76	35.75	4.76	40.76	5.54	"	
Mesitylene	C_9H_{12}	120.0	20.	0.8558	1.4912	68.87	8.35	40.60	4.85	46.19	5.43	Brühl.	
Cumene	"	"	12.	0.8432	1.4801	68.33	7.81	40.43	4.68	46.16	5.40	Gladstone.	
Cymene	$C_{10}H_{14}$	134.0	22.6	0.8530	1.4847	74.16	7.81	45.00	4.57	51.28	5.12	Brühl.	B. P. 175°–176°.
						Mean..	8.08		4.80		5.47		

TABLE I.—*Continued.*

Substance.	Formula.	Mol. weight.	Temperature.	Spec. grav. at $t°/4°$.	Index of refraction for ray D.	Molecular refraction, $\frac{P(M-1)}{D}$	Difference for CH_2.	Molecular refraction, $\frac{P(M-1)}{(M^2+2)D}$	Difference for CH_2.	Molecular refraction, $\frac{P(M-1)}{MD}$	Difference for CH_2.	From the data of	Remarks.
						B: Alcohols.							
Methyl	CH_4O	32.0	18.0°	0.7961	1.3301	13.27		8.14		9.94		Gladstone.	
Ethyl	C_2H_6O	46.0	20.	0.7887	1.36164	21.09	7.82	12.92	4.78	15.49	5.55	Ketteler.	
Propyl	C_3H_8O	60.0	"	0.8044	1.38543	28.75	7.66	17.35	4.43	20.75	5.26	Brühl.	
Isopropyl	"	"	"	0.7887	1.37757	28.72	7.63	17.53	4.61	20.85	5.36	"	
Butyl	$C_4H_{10}O$	74.0	"	0.8099	1.3991	36.47	7.72	22.10	4.57	26.06	5.31	"	
Isobutyl	"	"	"	0.8062	1.3959	36.34	7.62	22.04	4.51	26.03	5.18	Landolt.	
Isoamyl	$C_5H_{12}O$	88.0	"	0.8123	1.4078	44.18	7.84	26.69	4.65	31.38	5.35	"	
Phenol	C_6H_6O	94.0	21.	1.0598	1.5509	48.86		28.28		31.49		Gladstone.	
Cresol	C_7H_8O	108.0	23.	1.0390	1.5419	56.32	7.46	32.46	4.18	36.53	5.04	"	
m-Cresol	"	"	19.	1.0330	1.5364	56.08	7.22	32.63	4.35	36.50	5.01	"	
						Mean.	7.62		4.51		5.26		
						C: Aldehydes.							
Acetic	C_2H_4O	44.0	20.0°	0.7799	1.3316	18.71		11.56		14.05		Landolt.	*M* calculated.
Propionic	C_3H_6O	58.0	"	0.8066	1.3636	26.15	7.44	16.01	4.45	19.17	5.17	Brühl.	
Butyric	C_4H_8O	72.0	"	0.8170	1.3843	33.87	7.72	20.62	4.61	24.47	5.30	"	
Isobutyric	"	"	"	0.7938	1.3730	33.83	7.68	21.36	5.35	24.63	5.46	"	
Valeric	$C_5H_{10}O$	86.0	"	0.7984	1.3882	41.80	7.98	25.43	4.07	30.12	5.49	Landolt.	*M* calculated.
Heptoic	$C_7H_{14}O$	114.0	"	0.8495	1.4257	57.13	7.66	34.36	4.47	40.08	4.98	Brühl.	
						Mean..	7.70		4.59		5.27		
						D: Acids.							
Formic	CH_2O_2	46.0	20.0°	1.2188	1.3714	14.02		8.57		10.22		Landolt.	*M* calculated.
Acetic	$C_2H_4O_2$	60.0	"	1.0495	1.3718	21.26	7.24	12.98	4.41	15.49	5.27	"	" "
Propionic	$C_3H_6O_2$	74.0	"	0.9946	1.3866	28.76	7.50	17.49	4.51	20.74	5.25	"	" "
Butyric	$C_4H_8O_2$	88.0	"	0.9587	1.3979	36.52	7.76	22.47	4.98	26.12	5.38	Brühl.	
Isobutyric	"	"	"	0.9490	1.3930	36.44	7.68	22.13	4.64	26.03	5.29	"	
Isovaleric	$C_5H_{10}O_2$	102.0	"	0.9298	1.4043	44.36	7.92	26.85	4.72	31.52	5.49	Landolt.	*M* calculated.
Isocaproic	$C_6H_{12}O_2$	116.0	"	0.9237	1.4138	51.96	7.60	31.37	4.52	36.74	5.22	"	" "
Heptoic	$C_7H_{14}O_2$	130.0	"	0.9160	1.4215	59.81	7.85	36.02	4.65	42.08	5.34	"	" "
						Mean..	7.67		4.63		5.32		

TABLE I.—*Continued.*

Substance.	Formula.	Mol. weight.	Temperature.	Spec. grav. at t°/4°.	Index of refraction for ray D.	Molecular refraction, $\frac{P(M-1)}{D}$	Difference for CH_2.	Molecular refraction, $\frac{P(M-1)}{(M+2)D}$	Difference for CH_2.	Molecular refraction, $\frac{P(M-1)}{MD}$	Difference for CH_2.	From the data of	Remarks.
E: Ethereal Salts.													
Methyl formate.....	$C_2H_4O_2$	60.0	20.0°	0.9694	1.3438	21.28		13.07		15.83		J. H. Long.	B. P. 32.8° (P. 735 mm.)
Ethyl "	$C_3H_6O_2$	74.0	"	0.9064	1.3599	29.38	8.10	18.01	4.94	21.60	5.57	Landolt.	*M* calculated.
Propyl "	$C_4H_8O_2$	88.0	"	0.8962	1.3775	37.07	7.67	22.67	4.60	26.91	5.31	J. H. Long.	B. P. 67° (P. 431 mm.)
Isobutyl "	$C_5H_{10}O_2$	102.0	"	0.8657	1.3874	45.64	8.57	27.70	5.09	32.82	5.91	"	" 99° (P. 735 mm.)
Amyl "	$C_6H_{12}O_2$	116.0	"	0.8832	1.3980	52.32	6.68	32.03	4.33	37.42	4.60	Landolt.	*M* calculated.
Methyl acetate.....	$C_3H_6O_2$	74.0	"	0.9039	1.3610	29.53	8.25	18.09	5.02	21.69	5.86	"	" "
Ethyl "	$C_4H_8O_2$	88 0	"	0.9007	1.3726	36.34	6.81	22.24	4.15	26.47	4.78	"	" "
							6.96		4.23		4.87		
Propyl "	$C_5H_{10}O_2$	102.0	"	0.8856	1.3844	44.27	7.93	26.91	4.71	31.97	5.50	Brühl.	B. P. 100°.
							7.20		4.30		5.06		
Ethyl butyrate.....	$C_6H_{12}O_2$	116.0	"	0.8906	1.3960	51.50	7.23	31.30	4.39	36.89	4.92	J. H. Long.	" 114° (P. 735 mm.)
							5.86		3.60		4.07		
Amyl acetate.....	$C_7H_{14}O_2$	130.0	"	0.8561	1.4038	61.36	9.86	37.12	5.82	43.71	6.82	Landolt.	*M* calculated.
							9.04		5.09		6.29		
Methyl propionate..	$C_4H_8O_2$	88.0	"	0.9246	1.3776	35.94	6.41	21.92	3.83	26.09	4.40	J. H. Long.	B. P. 79.5° (P. 735 mm.)
							6.56		3.91		4.49		
Ethyl " ..	$C_5H_{10}O_2$	102.0	"	0.8904	1.3842	44.01	8.07	26.57	4.65	31.79	5.70	"	" 81.5° (P. 402 mm.)
							7.67		4.33		5.22		
Propyl " ..	$C_6H_{12}O_2$	116.0	"	0.8828	1.3935	51.71	7.70	31.30	4.73	37.11	5.32	"	" 101.5° (P. 384 mm.)
							7.44		4.39		5.14		
Isobutyl " ..	$C_7H_{14}O_2$	130.0	"	0.8694	1.3975	59.43	7.72	36.05	4.75	42.53	5.41	"	" 135.5° (P. 735 mm.)
Amyl " ..	$C_8H_{16}O_2$	144.0	"	0.8703	1.4065	67.27	7.84	40.80	4.75	47.79	5.26	"	" 159.5°(")
							8.91		3.68		4.08		
Methyl butyrate	$C_5H_{10}O_2$	102.0	"	0.8976	1.3889	44.17	8.23	26.87	4.95	31.80	5.71	"	" 103.5°(")
							7.83		4.63		5.33		
" isobutyrate..	"	"	"	0.8893	1.3840	44.04	8.10	26.58	4.66	31.82	5.73	"	" 90.° (")
							7.70		4.34		5 35		
Ethyl butyrate.....	$C_6H_{12}O_2$	116.0	"	0.8906	1.3960	51.50	7.33	31.30	4.43	36.89	5.09	"	" 114.° (")
							7.49		4.73		5.10		
" isobutyrate..	"	"	"	0.8697	1.3880	51.75	7.71	31.47	4.89	37.29	5.47	"	" 107.° (")
							7.50		4.60		5.49		
Propyl " ..	$C_7H_{14}O_2$	130.0	"	0.8738	1.3959	58.90	7.15	35.71	5.24	42.19	4.90	"	" 130.5°(")
							7.40		4.41		5.30		

TABLE I.—*Continued.*

Substance.	Formula.	Mol. weight.	Temperature.	Spec. grav. at $t°/4°$.	Index of refraction for ray D.	Molecular refraction, $\frac{P(M-1)}{D}$	Difference for CH_2.	Molecular refraction, $\frac{P(M^2-1)}{(M^2+2)D}$	Difference for CH_2.	Molecular refraction, $\frac{P(n-1)}{MD}$	Difference for CH_2.	From the data of	Remarks.
Isobutyl butyrate ...	$C_8H_{16}O_2$	144.0	20.0°	0.8627	1.4045	67.52	8.62	40.87	5.16	48.07	5.88	J. H. Long.	B. P. 154.5°(P. 735 mm.)
							8.19		4.82		5.54		
Isobutyl isobutyrate	"	"	"	0.8575	1.3999	67.16	8.26	40.69	4.98	47.99	5.80	"	" 144.5°(")
							7.77		4.64		5.46		
Amyl butyrate.....	$C_9H_{18}O_2$	158.0	"	0.8646	1.4110	75.11	7.59	46.72	6.03	53.23	5.16	"	" 178.° (")
							7.95		5.85		5.24		
Amyl isobutyrate...	"	"	"	0.8580	1.4076	75.06	7.55	44.45	3.76	53.32	5.25	"	" 166.5°(")
							7.91		3.58		5.33		
Methyl valerate	$C_6H_{12}O_2$	116.0	"	0.8795	1.3948	51.97	7.93	31.60	5.02	37.26	5.46	Landolt.	*M* calculated.
							7.80		4.73		5.44		
Ethyl "	$C_7H_{14}O_2$	130.0	"	0.8661	1.3971	59.54	7.57	36.15	4.55	42.61	5.35	"	" "
							8.04		4.85		5.72		
Propyl "	$C_8H_{16}O_2$	144.0	"	0.8634	1.4036	67.32	7.78	40.75	4.60	47.96	5.35	J. H. Long.	B. P. 156.° (P. 735 mm.)
							8.42		5.04		5.77		
Isobutyl "	$C_9H_{18}O_2$	158.0	"	0.8558	1.4063	75.01	7.69	45.39	4.64	53.34	5.38	"	" 169.° (")
							7.49		4.70		5.27		
Amyl "	$C_{10}H_{20}O_2$	172.0	"	0.8568	1.4120	82.73	7.72	49.95	4.56	58.59	5.25	Landolt.	*M* calculated.
							7.62		3.23		5.36		
						Mean..	7.68		4.62		5.33		

Halogen Derivatives.

Propyl chloride	C_3H_7Cl	78.5	20.0°	0.8898	1.3886	34.28		20.84		24.69		Brühl.	
Isobutyl "	C_4H_9Cl	92.5	19.0°	0.8626	1.3979	42.67	8.39	25.87	5.03	30.52	5.83	Gladstone.	
Amyl "	$C_5H_{11}Cl$	106.5	20.0°	0.8740	1.4102	49.98	7.31	30.17	4.30	35.44	4.92	Jahn.	
Ethyl bromide.....	C_2H_5Br	109.0	"	1.4555	1.4239	31.74		19.48		22.29		Weegmann.	
Ethyl "	"	"	"	1.4569	1.4241	31.73		19.10		22.28		Haagen.	*M* calculated.
Propyl "	C_3H_7Br	123.0	"	1.3520	1.4339	39.47	7.74	23.68	4.58	27.53	5.25	Brühl.	
							7.73		4.20		5.24		
Isopropyl "	"	"	"	1.3097	1.4251	39.93	8.20	24.02	4.92	28.01	5.73	"	
							8.19		4.54		5.72		
Isoamyl "	$C_5H_{11}Br$	151.0	"	1.2202	1.4412	55.42	7.75	33.17	4.58	38.45	5.22	Haagen.	*M* calculated.
							7.98		4.74		5.46		
Methyl iodide.....	CH_3I	142.0	"	2.2582	1.5297	33.30		19.41		21.77		"	
Ethyl "	C_2H_5I	156.0	"	1.9305	1.5131	41.46	8.16	24.30	4.89	27.40	5.63	"	*M* calculated.
Propyl "	C_3H_7I	170.0	"	1.7427	1.5051	49.16	7.70	28.93	4.63	32.66	5.26	Brühl.	
Isopropyl "	"	"	"	1.7033	1.4997	49.86	8.40	29.34	5.04	33.25	5.85	"	
Butyl "	C_4H_9I	184.0	"	1.6166	1.5001	56.91	7.75	33.47	4.54	37.94	5.28	"	
Isobutyl "	"	"	"	1.6056	1.4960	56.78	6.92	33.47	4.13	37.99	4.74	"	
Amyl "	$C_5H_{11}I$	198.0	14.0°	1.5048	1.4960	65.26	8.48	38.43	4.96	43.62	5.63	Gladstone.	
						Mean .	7.90		4.64		5.41		

TABLE I.—*Continued.*

Substance.	Formula.	Mol. weight.	Temperature.	Spec. grav. at $t°/4°$.	Index of refraction for ray D.	Molecular refraction, $\frac{P(M-1)}{D}$	Difference for CH_2.	Molecular refraction, $\frac{P(M^2-1)}{(M+2)D}$	Difference for CH_2.	Molecular refraction, $\frac{P(M-1)}{MD}$	Difference for CH_2.	From the data of	Remarks.
F: Nitrogen Compounds.													
Propyl amine	C_3H_9N	59.0	23.5°	0.7140	1.3873	32.00		19.46		23.07		Gladstone.	
Diethyl "	$C_4H_{11}N$	73.0	19.0°	0.7092	1.3871	39.84	7.84	24.24	4.78	28.72	5.65	"	
Triethyl "	$C_6H_{15}N$	101.0	"	0.7317	1.4005	55.28	7.72	33.49	4.63	39.47	5.38	"	
Dipropyl "			23.2°	0.7356	1.4025	55.27	7.72	33.46	4.61	39.42	5.35	"	*M* calculated.
Tripropyl "	$C_9H_{21}N$	143.0	22.8°	0.7535	1.4171	80.15	8.29	47.71	4.75	56.56	5.71	"	
Aniline	C_6H_7N	93.0	13.0°	1.0160	1.5828	53.34		30.58		33.70		"	
o-Toluidine	C_7H_9N	107.0	20.0°	0.9986	1.5728	61.38	8.04	35.29	4.71	39.02	5.32	Brühl.	
Xylidine	$C_8H_{11}N$	121.0	19.0°	0.9867	1.5585	68.49	7.11	39.55	4.26	43.94	4.92	Gladstone.	
Propionitrile	C_3H_5N	55.0	"	0.7862	1.3681	25.75		15.76		18.92		"	
Valeronitrile	C_5H_9N	83.0	18.0°	0.8010	1.3917	40.59	7.42	24.65	4.45	29.16	5.12	"	
Capronitrile	$C_6H_{11}N$	97.0	"	0.8040	1.4087	49.31	8.72	29.81	5.16	35.00	5.84	"	
						Mean.	7.86		4.67		5.41		
G: Sulphur Compounds.													
Ethyl mercaptan	C_2H_6S	62.0	20.0°	0.8931	1.4306	29.89		17.96		20.89		Nasini.	
Isobutyl "	$C_4H_{10}S$	90.0	"	0.8357	1.4386	47.23	8.67	28.30	5.17	32.76	5.93	"	
Isoamyl "	$C_5H_{12}S$	104.0	"	0.8348	1.4412	54.96	7.73	32.91	4.61	38.38	5.62	"	
Ethyl sulphide	$C_4H_{10}S$	90.0	"	0.8368	1.4423	47.57	7.39	28.47	4.44	32.98	5.40	"	
Amyl "	$C_{10}H_{22}S$	174.0	"	0.8431	1.4524	93.37	7.63	55.71	4.54	64.28	5.21	"	
						Mean.	7.85		4.69		5.54		
H: Alcohols. (Ray Hα.)													
Water	H_2O	18.0	20.0°	0.99824	1.33155	5.96		3.69		4.48		Brühl.	
Methyl alcohol	CH_4O	32.0	"	0.7953	1.33789	13.19	7.23	8.16	4.47	9.93	5.45	"	
Ethyl "	C_2H_6O	46.0	"	0.8000	1.36054	20.73	7.54	12.71	4.55	15.23	5.30	"	
Propyl "	C_3H_8O	60.0	"	0.8044	1.38345	28.56	7.83	17.42	4.71	20.67	5.44	"	
Isopropyl "	"	"	"	0.8030	1.37938	28.34	7.61	17.44	4.73	20.54	5.31	"	
Butyl "	$C_4H_{10}O$	74.0	"	0.8099	1.39712	36.27	7.71	22.01	4.59	25.96	5.29	"	
Isobutyl "	"	"	"	0.8062	1.39395	36.16	7.82	21.96	4.52	25.94	5.49	"	
Trimethyl carbinol	"	"	"	0.7864	1.38572	36.30	7.74	22.13	4.71	26.27	5.60	"	
Amyl alcohol	$C_5H_{12}O$	88.0	"	0.8123	1.40573	43.95	7.79	26.62	4.61	31.26	5.39	"	
Methylhexylcarbinol	$C_8H_{18}O$	130.0	"	0.8193	1.42231	67.01	7.69	40.35	4.43	47.06	5.26	"	
						Mean.	7.66		4.59		5.37		

TABLE I.—*Continued.*

Substance.	Formula.	Mol. weight.	Temperature.	Spec. grav. at $t°/4°$.	Index of refraction for ray Ha.	Molecular refraction, $\frac{P(M-1)}{D}$.	Difference for CH_2.	Molecular refraction, $\frac{P(M^2-1)}{(M^2+2)D}$.	Difference for CH_2.	Molecular refraction, $\frac{P(M-1)}{MD}$.	Difference for CH_2.	From the data of	Remarks.
I: Aldehydes.													
Acetic	C_2H_4O	44.0	20.0°	0.7799	1.32975	18.61		11.50		13.99		Brühl.	
Propionic	C_3H_6O	58.0	"	0.8066	1.36157	26.00	7.39	15.93	4.43	19.10	5.11	"	
Butyric	C_4H_8O	72.0	"	0.8170	1.38222	33.68	7.65	20.52	4.59	24.36	5.26	"	
Isobutyric	"	"	"	0.7938	1.37094	33.64	7.64	20.56	4.63	24.46	5.36	"	
Valeric	$C_5H_{10}O$	86.0	"	0.7984	1.38614	41.60	7.96	25.31	4.75	29.99	5.63	"	
Heptylic	$C_7H_{14}O$	114.0	"	0.8495	1.42340	56.82	7.61	34.20	4.45	39.91	4.96	"	
						Mean..	7.66		4.57		5.26		
J: Acids.													
Formic	CH_2O_2	46.0	20.0°	1.2188	1.36927	13.94		8.52		10.28		Brühl.	
Acetic	$C_2H_4O_2$	60.0	"	1.0495	1.36985	21.55	7.61	12.93	4.41	15.44	5.16	"	
Propionic	$C_3H_6O_2$	74.0	"	0.9946	1.38460	28.62	7.07	17.42	4.49	20.66	5.22	"	
Butyric	$C_4H_8O_2$	88.0	"	0.9594	1.39554	36.28	7.66	22.01	4.59	25.99	5.33	"	
Isobutyric	"	"	"	0.9490	1.39093	36.25	7.63	22.03	4.61	26.06	5.40	"	
Isovaleric	$C_5H_{10}O_2$	102.0	"	0.9298	1.40220	44.12	7.87	26.72	4.69	31.45	5.39	"	
Isocaproic	$C_6H_{12}O_2$	116.0	"	0.9237	1.41164	51.70	7.58	31.22	4.50	36.62	5.17	"	
Heptoic	$C_7H_{14}O_2$	130.0	"	0.9160	1.41923	59.50	7.80	35.85	4.63	41.92	5.30	"	
						Mean .	7.60		4.56		5.28		
K: Ethereal Salts.													
Ethyl formate	$C_3H_6O_2$	74.0	20.0°	0.9664	1.35800	29.23		17.93		21.52		Brühl.	
Ethyl acetate	$C_4H_8O_2$	88.0	"	0.9007	1.37068	36.22	6.99	22.14	4.21	26.42	4.90	"	
Propyl "	$C_5H_{10}O_2$	102.0	"	0.8856	1.3824	44.04	7.82	26.83	4.69	31.86	5.44	"	
Ethyl butyrate	$C_6H_{12}O_2$	116.0	"	0.8892	1.39404	51.41	7.37	31.20	4.37	36.85	4.99	"	
Ethyl valerate	$C_7H_{14}O_2$	130.0	"	0.8861	1.39500	59.28	7.87	35.98	4.78	42.51	5.66	"	
Methyl acetate	$C_3H_6O_2$	74.0	"	0.9039	1.35915	29.41	7.47	18.03	4.49	21.63	5.22	"	
Ethyl "	$C_4H_8O_2$	88.0	"	0.9007	1.37068	36.22	6.81	22.14	4.11	26.42	4.79	"	
Propyl "	$C_5H_{10}O_2$	102.0	"	0.8856	1.3824	44.04	7.82	26.83	4.69	31.86	5.44	"	
Ethyl benzoate	$C_9H_{10}O_2$	150.0	"	1.0473	1.50104	71.76	7.69	42.20	4.65	47.80	5.44	Landolt.	
Methyl "	$C_8H_8O_2$	136.0	"	1.0862	1.51158	64.07		37.55		42.36		"	
						Mean..	7.48		4.50		5.24		

If each division of table I be treated similarly for each of the three formulæ we shall have average differences for CH_2, as given in table II. (Division *G* is omitted.)

TABLE II.

Division.	For $\frac{P(M-1)}{D}$	For $\frac{P(M^2-1)}{D(M^2+2)}$	For $\frac{P(M-1)}{MD}$
A, paraffins	7.74	4.56	5.25
" aromatic	8.00	4.75	5.44
B, paraffins	7.68	4.62	5.28
" aromatic	7.48	4.45	5.14
C, paraffins	7.69	4.58	5.24
D, "	7.65	4.61	5.31
E, "	7.68	4.62	5.34
" chlorides	7.87	4.65	5.39
" bromides	7.89	4.60	5.39
" iodides	7.94	4.69	5.37
F, paraffins	8.15	4.69	5.50
" aromatic	7.72	4.58	5.27
" nitriles	7.85	4.68	5.36
Mean for sodium light	7.77	4.62	5.33
H, paraffins	7.65	4.58	5.35
I, "	7.65	4.56	5.22
J, "	7.60	4.56	5.31
K "	7.50	4.51	5.25
Mean for red hydrogen light	7.60	4.55	5.28
Mean for the paraffins of *B*, *C*, *D*, *and E*	7.68	4.61	5.29

The comparison of the mean values for CH_2 of groups *H*, *I*, *J*, and *K*, with those of the like compound in groups *B*, *C*, *D*, and *E*, show higher numbers for sodium light in each case, but higher for the Gladstone and Lorentz-Lorenz formulæ than for the formula $\frac{P(M-1)}{MD}$. That this result is consistent with the three formulæ will appear from a brief consideration of them.

Consider the Gladstone formula for the same substance at the same temperature. We have $(M-1)K$, where K is a constant equal to P/D; let $M=1+x$, then $(M-1)K=Kx$, from which we determine that the molecular refraction varies with x.

In all ordinary cases x is greater for sodium light than for red hydrogen light. An inspection of the numbers in divisions *H*, *I*, *J*, and *K*, as compared with corresponding numbers in divisions *B*, *C*, *D*, and *E* of table I, shows that this is true in practice, as shown by the molecular refraction. We should then expect to find the differences for CH_2 to be a little greater for the paraffins of divisions *B*, *C*, *D*, and *E*, then for divisions *H*, *I*, *J*, and *K* of table I. An inspection of table II shows this to be the case.

If we consider the Lorentz-Lorenz formula in the same way we have $\frac{(1+x^2)-1}{(1+x^2)+2}K = K\frac{2+x}{2+x+3/x} = \frac{1}{1+\frac{3}{2x+x^2}}K$, which shows that the molecular refraction is greater in the case of sodium light, where x is greater, than for red hydrogen light.

A comparison of the indices of refraction of like substances in divisions *B* and *H* and *D* and *J* show that x is about 0.002 more for sodium light than for red hydrogen light. This difference will affect $\frac{3}{2x+x^2}$ more in the case of the alcohols than in the case of the acids since x is smaller in the case of the alcohols.

From this table we have 4.58 for ray Hα and 4.62 for ray *D* for the alcohols, and 4.56 for ray Hα and 4.61 for ray D for the acids. This discrepancy is explained by the fact that there are more alcohols compared in group *H* than in group *B*.

In the same way we have for the formula $\frac{P(M-1)}{MD}$, $K\frac{x}{1+x} = K\frac{1}{1+\frac{1}{x}}$ which shows that the greater the value of x the greater will be the molecular refraction, and the less the influence of the increment of 0.002 in the index of refraction.

Determination of Atomic Refraction.

Carbon, Hydrogen, and Oxygen.

In the determination of the values for atomic refraction, the values 7.68 for the Gladstone formula, 4.61 for the Lorentz-Lorenz formula, 5.29 for the formula $\frac{P(M-1)}{MD}$ will be as-

sumed as representing the difference in the molecular refraction for a difference of CH_2 in the molecule. It will be observed that these numbers are the averages given in table II for the paraffins of groups *B*, *C*, and *D*, and the first division of group *E*.

The acids may be considered as $n(CH_2)$ + carbonyl and hydroxyl oxygen. If $n \times 7.68$ for the Gladstone formula, $n \times 4.61$ for the Lorentz-Lorenz formula, and $n \times 5.29$ for the formula $\frac{P(M-1)}{MD}$, be subtracted from the molecular refraction of the acids the difference will stand for the oxygen of the group $O=C\angle O-H$. Table III shows these differences and gives an average of 5.95 for the Gladstone formula, 3.81 for the Lorentz-Lorenz formula, and 4.97 for my formula.

The aldehydes may be considered as $n(CH_2)$ + carbonyl oxygen. If, then, $n \times 7.68$, $n \times 4.61$, and $n \times 5.29$ be subtracted from the numbers representing the corresponding molecular refractions of the aldehydes the difference will stand for carbonyl oxygen.

Table IV shows these differences and gives an average of 3.25 for the Gladstone, 2.35 for the Lorentz-Lorenz and 3.38 for my formula.

The difference between the numbers standing for oxygen of the group $O=C\angle O-H$ and that of the group $=C=O$ will stand for the oxygen of the group $\equiv C-O-H$. Making the subtraction we find 2.70 for the Gladstone formula, 1.46 for the Lorenz formula, and 1.59 for my formula.

The alcohols may be considered as $n(CH_2)$ + hydroxyl oxygen + 2H. If, then, $n \times 7.68 + 2.70$, $n \times 4.61 + 1.46$, and $n \times 5.29 + 1.59$ be subtracted from the molecular refraction of the alcohols the difference will stand for 2H for the corresponding formula. Table V shows these differences and gives an average of 3.00 for the Gladstone formula, 2.16 for the Lorentz-Lorenz formula, and 3.28 for the formula $\frac{P(M-1)}{MD}$. The values for hydrogen are, then, 1.50, 1.08, and 1.64, and, therefore, the values for carbon are $7.68-3.00=4.68$; $4.61-2.16=2.45$; and $5.29-3.28=2.01$; for the three formulæ in the order observed in the columns of the tables.

TABLE III.—*Acids.*

Substance.	Formula $\frac{P(M-1)}{D}$			Formula $\frac{P(M^2-1)}{D(M^2+2)}$			Formula $\frac{P(M-1)}{DM}$		
	Molecular refraction.	$n \times 7.68$.	Difference 2O.	Molecular refraction.	$n \times 4.61$.	Difference 2O.	Molecular refraction.	$n \times 5.29$.	Difference 2O.
Formic	14.02	7.68	6.34	8.57	4.61	3.96	10.22	5.29	4.93
Acetic	21.26	15.36	5.90	12.98	9.22	3.76	15.49	10.58	4.91
Propionic	28.76	23.04	5.72	17.49	13.83	3.66	20.74	15.87	4.87
Butyric	36.52	30.72	5.80	22.47	18.44	4.03	26.12	21.16	4.96
Isovaleric	44.36	38.40	5.96	26.85	23.05	3.80	31.52	26.45	5.07
Isocaproic	51.96	46.08	5.88	31.37	27.66	3.71	36.74	31.74	5.00
Heptoic	59.81	53.76	6.05	36.02	32.27	3.75	42.08	37.03	5.05
Mean			5.95			3.81			4.97

TABLE IV.—*Aldehydes.*

Substance.	Formula $\frac{P(M-1)}{D}$			Formula $\frac{P(M^2-1)}{D(M^2+2)}$			Formula $\frac{P(M-1)}{MD}$		
	Molecular refraction.	$n \times 7.68$.	Difference O.	Molecular refraction.	$n \times 4.61$.	Difference O.	Molecular refraction.	$n \times 5.29$.	Difference O.
Acetic	18.71	15.36	3.35	11.56	9.22	2.34	14.05	10.58	3.47
Propionic	26.15	23.04	3.11	16.01	13.82	2.18	19.17	15.87	3.30
Butyric	33.87	30.72	3.15	20.62	18.44	2.18	24.47	21.16	3.31
Isobutyric	33.83	"	3.11	21.36	18.44	2.92	24.63	21.16	3.47
Valeric	41.81	38.40	2.41	25.43	23.05	2.38	30.12	26.45	3.67
Heptoic	57.13	53.76	3.37	34.36	32.27	2.09	40.08	37.03	3.05
Mean			3.25			2.35			3.38

TABLE V.—*Alcohols.*

Substance.	Formula $\frac{P(M-1)}{D}$			Formula $\frac{P(M^2-1)}{D(M^2+2)}$			Formula $\frac{P(M-1)}{MD}$		
	Molecular refraction.	$N(7.68)+2.70$.	Difference 2H.	Molecular refraction.	$N(4.61)+1.46$.	Difference 2H.	Molecular refraction.	$N(5.29)+1.59$.	Difference 2H.
Methyl	13.27	10.38	2.89	8.14	6.07	2.07	9.94	6.88	3.06
Ethyl	21.09	18.06	3.03	12.92	10.68	2.24	15.49	12.17	3.32
Propyl	28.75	25.74	3.01	17.35	15.29	2.06	20.75	17.46	3.29
Isopropyl	28.72	"	2.98	17.53	"	2.24	20.85	"	3.39
Butyl	36.47	33.42	3.05	22.10	19.90	2.20	26.06	22.75	3.31
Isobutyl	36.34	"	2.92	22.04	"	2.14	26.03	"	3.28
Isoamyl	44.18	41.10	3.08	26.69	24.51	2.18	31.38	28.04	3.34
Mean			3.00			2.16			3.28

I desire to call attention to the close approximation of the separate differences for 2O in table III to the mean for each

of the formulæ. A like comparison in the cases of O and 2H of tables IV and V is also desirable.

It has probably already been noted by the reader that the number obtained for hydrogen for the Gladstone formula is considerably larger than has been found for that element heretofore, and that the number for carbon is considerably less than has been found for that element. The number found by subtracting $n \times 7.68$ from the molecular refraction of the hydrocarbons of division A of table I is a number somewhat higher even than this. These numbers appear in table VI.

TABLE VI.—*Hydrocarbons.*

Substance.	Formula $\frac{P(M-1)}{D}$			Formula $\frac{P(M^2-1)}{D(M^2+2)}$			Formula $\frac{P(M-1)}{MD}$		
	Molecular refraction.	$n \times 7.68$.	Difference 2H.	Molecular refraction.	$n \times 4.61$.	Difference 2H.	Molecular refraction.	$n \times 5.29$.	Difference 2H.
Pentane	41.26	38.40	2.86	25.27	23.05	2.22	30.24	26.45	3.79
"	41.76	"	3.36	25.85	"	2.80	30.74	"	4.29
Hexane	49.11	46.08	3.03	29.84	27.66	2.18	35.36	31.74	3.62
"	49.03	"	2.95	30.01	"	2.35	36.04	"	4.30
Heptane	56.04	53.76	2.28	34.20	32.27	1.93	40.22	37.03	3.19
"	56.90	"	3.14	34.53	"	2.26	40.79	"	3.76
"	56.81	"	3.05	34.51	"	2.24	40.82	"	3.79
"	56.89	"	3.13	34.55	"	2.28	40.95	"	3.92
Octane	64.40	61.44	2.96	38.92	36.88	2.14	45.62	42.32	3.30
Nonane	72.19	69.12	3.07	43.39	41.49	1.90	50.82	47.61	3.21
Decane	79.99	76.80	3.15	48.08	46.10	1.98	56.07	52.90	3.17
Undecane	87.67	84.48	3.19	52.62	50.71	1.91	61.27	58.19	3.08
Dodecane	95.54	92.16	3.38	57.29	55.32	1.97	66.52	63.48	3.04
Tridecane	103.78	99.84	3.84	61.81	59.93	1.88	71.95	68.77	3.23
Tetradecane	111.67	107.52	4.15	66.71	64.54	2.17	77.08	74.06	3.02
Pentadecane	118.51	115.20	3.31	70.79	69.15	1.64	81.86	79.35	5.51
Hexadecane	126.33	122.88	3.45	75.37	73.76	1.61	86.78	84.64	2.14
Mean			3.20			2.08			3.37

This table shows 1.60, 1.04, and 1.68 for hydrogen; and 4.48, 2.53, and 1.92 for carbon, for the three formulæ, the numbers being in the order of the arrangements observed in the tables. It was pointed out near the beginning of the paper that these hydrocarbons could not be considered pure, and I, therefore, do not rely on the numbers obtained for hydrogen and carbon from table VI, but use them to show that the numbers obtained from the oxygen compounds agree very well with those obtained from the hydrocarbons themselves. If these hydrocarbons were pure, then I should have

depended on these numbers and should have used them in determining hydroxyl oxygen instead of using hydroxyl oxygen to obtain numbers for hydrogen.

Before making closer comparisons I wish to make a comparison similar to that of tables III, IV, and V, using numbers obtained from the use of red hydrogen light. In this comparison the numbers 7.60, 4.55, and 5.28 will be used as representing CH_2 for the three formulæ in the usual order. It will be observed that they are the average differences for CH_2 in groups *H*, *I*, *J*, and *K* of table I, as shown in table II.

These comparisons are shown in tables VII, VIII, and IX.

TABLE VII.—*Acids.*

Substance.	Formula $\frac{P(M-1)}{D}$			Formula $\frac{P(M^2-1)}{D(M^2+2)}$			Formula $\frac{P(M-1)}{MD}$		
	Molecular refraction.	$n \times 7.60$.	Difference 20.	Molecular refraction.	$n \times 4.55$.	Difference 20.	Molecular refraction.	$n \times 5.28$.	Difference 20.
Formic	13.94	7.60	6.34	8.52	4.55	3.97	10.28	5.28	5.00
Acetic	21.55	15.20	6.35	12.93	9.10	3.83	15.44	10.56	4.88
Propionic	28.62	22.80	5.82	17.42	13.65	3.77	20.66	15.84	4.82
Butyric	36.28	30.40	5.88	22.01	18.20	3.81	25.99	21.12	4.87
Isobutyric	36.25	"	5.85	22.03	"	3.83	26.06	"	4.94
Isovaleric	44.12	38.00	6.12	26.72	22.75	3.97	31.45	26.40	5.05
Isocaproic	51.70	45.60	6.10	31.22	27.30	3.92	36.62	31.68	4.94
Heptoic	59.50	53.20	6.30	35.85	31.85	4.00	41.92	36.96	4.96
Mean			6.09			3.89			4.93

TABLE VIII.—*Aldehydes.*

Substance.	Formula $\frac{P(M-1)}{D}$			Formula $\frac{P(M^2-1)}{D(M^2+2)}$			Formula $\frac{P(M-1)}{MD}$		
	Molecular refraction.	$n \times 7.60$.	Difference O.	Molecular refraction.	$n \times 4.55$.	Difference O.	Molecular refraction.	$n \times 5.28$.	Difference 20.
Acetic	18.61	15.20	3.41	11.50	9.10	2.40	13.99	10.56	3.44
Propionic	26.00	22.80	3.20	15.73	13.65	2.26	19.10	15.84	3.26
Butyric	33.68	30.40	3.18	20.52	18.20	2.32	24.36	21.12	3.24
Isobutyric	33.63	"	3.24	20.56	"	2.34	24.46	"	3.34
Valeric	41.60	38.00	3.60	25.31	22.74	2.56	29.99	26.40	3.59
Heptoic	56.80	53.20	3.60	34.20	31.85	2.35	39.91	36.96	2.95
			3.37			2.37			3.30

This shows 2.72, 1.52, and 1.63 for hydroxyl oxygen for the three formulæ taken in the usual order.

TABLE IX.—*Alcohols.*

Substance.	Formula $\frac{P(M-1)}{D}$			Formula $\frac{P(M^2-1)}{D(M+2)}$			Formula $\frac{P(M-1)}{MD}$		
	Molecular refraction.	$n \times 7.60 + 2.72$.	Difference 2H.	Molecular refraction.	$n \times 4.55 + 1.32$.	Difference 2H.	Molecular refraction.	$n \times 5.28 + 1.63$.	Difference 2H.
Methyl	13.19	10.32	2.87	8.16	6.07	2.09	9.93	6.91	3.02
Ethyl	20.73	17.92	2.81	12.71	10.62	2.09	15.23	12.18	3.04
Propyl	28.56	25.52	3.04	17.42	15.17	2.25	20.67	17.47	3.20
Isopropyl	28.34	25.52	2.82	17.44	15.17	2.27	20.54	17.47	3.07
Butyl	36.27	33.12	3.15	22.01	19.72	2.29	25.96	22.75	3.21
Isobutyl	36.16	33.12	3.04	21.96	19.72	2.24	25.94	22.75	3.19
Amyl	43.95	40.72	3.23	26.62	24.27	2.35	31.26	28.03	3.23
Mean			2.99			2.22			3.28

From tables III, IV, and V, and tables VII, VIII, and IX, we have for the

	Carbon.	Hydrogen.	Carbonyl oxygen.	Hydroxyl oxygen.
Gladstone formula for sodium light	4.68	1.50	3.25	2.70
" red hydrogen light	4.61	1.50	3.26	2.72
Lorentz-Lorenz formula for sodium "	2.45	1.08	2.35	1.46
" red hydrogen light	2.33	1.11	2.37	1.52
Formula $\frac{P(M-1)}{MD}$ for sodium light	2.01	1.64	3.38	1.59
" red hydrogen light	2.00	1.64	3.30	1.63

Ostwald, in the second edition of his *Lehrbuch der Allgemeinen Chemie*, pages 432–3, under investigations by Landolt, gives Landolt's numbers for carbon and hydrogen for the Gladstone formula in the following manner:

Substance.	Molecular refraction.	Difference C.	Substance.	Molecular refraction.	Difference 2H.
Aldehyde	18.58	....	Ethyl alcohol	20.70	....
Methyl alcohol	13.24	5.44	Aldehyde	18.58	2.12
Acetone	26.12	....	Propyl alcohol	28.30	....
Ethyl alcohol	20.17	5.42	Acetone	26.12	2.18
Valeric aldehyde	41.54	....	Amyl alcohol	43.81	....
Butyl alcohol	36.11	5.43	Valeric aldehyde	41.54	2.35
Propionic acid	28.57	....	Ethylene alcohol	23.77	....
Ethylene alcohol	23.77	4.80	Acetic acid	21.11	2.66
Acetic anhydride	36.56	....	Glycerol	34.32	....
Lactic acid	31.81	4.75	Lactic acid	31.81	2.51

On page 433 he shows that if $n \times 7.60$ be subtracted from the molecular refraction of the acids, the mean difference is 6.00 which gives a mean value of 3.00 for oxygen. He then

obtains a mean value of 2.60 for 2H by subtracting $n \times 7.60 + 3.00$ from the molecular refraction of the alcohols. On pages 436–7, under investigations by Brühl, he shows that hydroxyl oxygen has one value, 2.75, and carbonyl oxygen another, 3.40, and gives in the table of atomic refractions carbonyl oxygen 3.40 and hydroxyl oxygen 2.80. If the number 2.75 instead of 3.00 had been used in finding a value for 2H from the alcohols, a value of 2.85 instead of 2.60 would have been found for 2H, and of 4.75 instead of 5.00 for carbon.

It seems strange that this chance for a different value for hydrogen and therefore for carbon was not noticed by Ostwald and others, especially as Landolt, in the paper[1] abstracted by Ostwald, after giving the values 5.00 for carbon, 1.30 for hydrogen, and 3.00 for oxygen, calls attention to the close agreement of numbers obtained for carbon from diamond and for hydrogen and oxygen obtained from the gases. These numbers were 4.85 for carbon, 1.54 for hydrogen, and 3.04 for oxygen. This number for hydrogen is very close to the one found for hydrogen in this paper.

For the oxygen numbers found in this paper there is a difference between the values of hydroxyl and carbonyl oxygen of 0.55 for the Gladstone formula; of 0.89 for the Lorentz-Lorenz formula; and of 1.79 for my formula. For red hydrogen light there is a difference, in the same order, of 0.55, 0.85, and 1.67.

At the beginning of this paper I pointed out that there was a larger difference for the value of CH_2 obtained by comparing ethereal salts and acids than by comparing like compounds. I have since discovered Conrady's calculations[2] from which he obtains the following values for sodium light for the Lorentz-Lorenz formula: hydroxyl oxygen, 1.521; carbonyl oxygen, 2.87; ether oxygen, 1.683. The difference between 1.521 and 1.683 is too small a value to be of any practical use but agrees with the difference found by me in the paper before mentioned. Of course the figures of the third decimal place may be entirely ignored in all of Conrady's numbers.

Conrady in the same paper distinguishes carbon as carbon

[1] Pogg. Ann. der Phys., **123**, 623 (1864).
[2] Ztschr. phys. chem., **3**, 210 (1889).

standing alone, and carbon in combination with carbon. In the preceding tables methyl alcohol, formic acid, and methyl salts are examples of carbon standing alone. To carbon standing alone and designated by C° he gives the value 2.592, and to carbon in combination with carbon and designated by C′ he gives the value 2.501 for sodium light.

Tables X and XI which follow show a decided difference between hydroxyl oxygen and ether oxygen for my formula, but do not for either of the others. Table XII shows that, on the average, carbon standing alone has a higher value than carbon in combination with carbon, but on the whole leaves the matter in a somewhat doubtful state.

TABLE X.—*Ethereal Salts.*

Substance.	Formula $\frac{P(M-1)}{D}$			Formula $\frac{P(M^2-1)}{D(M^2+2)}$			Formula $\frac{P(M-1)}{MD}$		
	Molecular refraction.	$n \times 7.68$.	Difference 2O.	Molecular refraction.	$n \times 4.61$.	Difference 2O.	Molecular refraction.	$n \times 5.99$.	Difference 2O.
Ethyl formate	29.38	23.04	6.34	18.01	13.92	4.09	21.60	15.87	5.73
Propyl "	37.07	30.72	6.35	22.61	18.56	4.05	26.91	21.16	5.75
Amyl "	52.32	46.08	6.24	32.03	27.84	4.19	37.42	31.74	5.68
Methyl acetate	28.53	23.04	6.49	18.09	13.92	4.17	21.69	15.87	5.82
Ethyl "	36.34	30.72	5.62	22.24	18.56	3.68	26.47	21.16	5.31
Propyl "	44.27	38.40	5.87	26.91	23.20	3.71	31.97	26.42	5.52
Methyl propionate	35.94	30.72	5.22	21.92	18.56	3.36	26.09	21.16	4.93
Ethyl "	44.01	38.40	5.64	26.57	23.20	3.38	31.79	26.45	5.34
Amyl "	67.27	61.44	5.83	40.80	37.12	3.68	47.79	42.32	5.47
Methyl butyrate	44.04	38.40	5.64	26.58	23.20	3.38	31.82	26.45	5.37
Ethyl "	51.50	46.08	5.38	31.30	27.84	3.46	36.89	31.74	5.15
Amyl "	75.11	69.14	5.97	46.72	41.76	4.96	53.23	47.61	5.62
Methyl valerate	51.97	46.08	5.89	31.60	27.84	3.76	37.26	31.74	5.52
Ethyl "	59.54	53.76	5.78	36.15	32.48	3.67	42.61	37.03	5.58
Amyl "	82.73	76.80	5.93	49.95	46.50	3.45	58.59	52.90	5.69
Mean			5.88			3.78			5.50

The average 5.88 is only 0.07 below 5.95, the average difference of table III, and only five of the differences of table X are above 5.95. The average 3.78 is only 0.03 below that found in table III, and again only five of the differences of table X are above 3.81. The average 5.50 is 0.53 above 4.97, the average of table III, and with the exception of methyl propionate all the differences are above 4.97.

Table XI.

Substance.	$\frac{P(M-1)}{D}$	Diff. CH_2.	$\frac{P(M^2-1)}{D)M^2+2)}$	Diff. CH_2.	$\frac{P(M-1)}{MD}$	Diff. CH_2.
Methyl formate	21.28	....	13.07	....	15.83	....
Formic acid	14,02	7.26	8.57	4.50	10.22	5.61
Ethyl formate	29.38	....	18.01	....	21.60	....
Acetic acid	21.26	8.12	12.98	5.03	15.49	6.11
Propyl formate	37.07	....	22.61	....	26.91	....
Propionic acid	28.76	8.31	17.49	5.12	20.74	6.17
Isobutyl formate	45.64	....	27.70	....	32.82	6.79
Isobutyric acid	36.44	9.20	22.13	5.57	26.03	....
Amyl formate	52.32	....	32.03	....	37.42	....
Valeric acid	44.36	7.96	26.85	5.18	31.52	5.90
Methyl acetate	29.53	....	18.09	....	21.69	....
Acetic acid	21.26	8.27	12.98	5.11	15.49	6.20
Ethyl acetate	36.34	....	22.24	....	26.47	....
Propionic acid	28.76	7.58	17.49	4.75	20.74	5.63
Propyl acetate	44.27	....	26.91	....	31.97	....
Butyric acid	36.52	7.75	22.47	4.44	26.12	5.85
Methyl propionate	35.94	....	21.92	....	26.09	....
Propionic acid	28.76	7.18	17.49	4.43	20.74	5.35
Ethyl propionate	44.01	....	29.57	....	31.79	....
Butyric acid	36.52	7.49	22.47	4.10	26.12	5.67
Propyl propionate	51.71	....	31.30	....	37.11	....
Valeric acid	44.36	7.35	26.85	4.45	31.52	5.59
Isobutyl propionate	59.43	....	36.05	....	42.53	....
Caproic acid	51.96	7.47	31.37	4.68	36.74	5.79
Amyl propionate	67.27	....	40.80	....	47.79	....
Heptoic acid	59.81	7.46	36.02	4.78	42.08	5.71
Methyl butyrate	44.17	....	26.87	....	31.80	....
Butyric acid	36.52	7.65	22.47	4.40	26.12	5.68
Methyl isobutyrate	44.04	....	26.58	....	31.82	....
Isobutyric acid	36.44	7.60	22.13	4.45	26.03	5.79
Ethyl isobutyrate	51.75	....	31.47	....	37.28	....
Valeric acid	44.36	7.39	26.85	4.62	31.52	5.77
Propyl isobutyrate	58.90	....	35.71	....	42.19	....
Caproic acid	51.96	6.94	31.37	4.34	36.74	5.45
Isobutyl butyrate	67.52	....	40.87	....	48.07	....
Heptoic acid	59.81	7.71	36.02	4.85	42.08	5.99

Substance.	$\frac{P(M-1)}{D}$	Diff. CH_2.	$\frac{P(M^2-1)}{D(M^2+2)}$	Diff. CH_2.	$\frac{P(M-1)}{MD}$	Diff. CH_2.
Methyl valerate.....	51.97	....	31.60	....	37.26	....
Valeric acid.....	44.36	7.61	26.85	4.75	31.52	5.74
Ethyl valerate.....	59.54	....	36.15	....	42.61	....
Caproic acid.....	51.96	7.28	31.37	4.78	36.74	5.87
Propyl valerate.....	67.32	....	40.76	....	47.96	....
Heptoic acid.....	59.81	7.51	36.02	4.73	42.08	5.88
Mean.....		7.68		4.72		5.84

In table XI the average difference for the Gladstone formula, 7.68, is the same as shown in table II. Fourteen of the twenty-one differences are below 7.68. The average difference for the Lorentz-Lorenz formula is 0.11 above 4.61; this agrees with Conrady's calculations very closely. Thirteen of the twenty-one differences are above 4.61, while only eight are below. The average difference for my formula is 0.55 above 5.29, and all the differences of the table are above 5.29. This agrees very closely with the number found in table X. For my formula, then, ether oxygen $= 1.59 + 0.54 = 2.13$.

The first four differences of table X and the first six of table XI would seem to prove Conrady's proposition in regard to carbon standing alone. Both tables, however, contain a number of examples where it does not hold. Table XII also shows several examples where it does not hold, although more than half of the cases given in the table favor it.

The examples of table XII are taken from table I:

TABLE XII.

Substance.	$\frac{P(M-1)}{D}$	Diff. CH_2.	$\frac{P(M^2-1)}{D(M^2+2)}$	Diff. CH_2.	$\frac{P(M-1)}{MD}$	Diff. CH_2.
Ethyl formate.....	29.38	....	18.01	....	21.60	....
Ethyl acetate.....	36.34	6.96	22.24	4.23	26.47	4.87
Amyl formate.....	52.32	....	32.03	....	37.42	....
Amyl acetate.....	61.36	9.04	37.12	5.09	43.71	6.29
Methyl formate.....	21.28	....	13.07	....	15.83	....
Ethyl formate.....	29.38	8.10	18.01	4.94	21.60	5.77
Propyl formate.....	37.07	....	22.61	....	26.91	....
Propyl acetate.....	44.27	7.20	26.91	4.30	31.97	5.06

Substance.	$\frac{P(M-1)}{D}$	Diff. CH_2.	$\frac{P(M^2-1)}{D(M^2+2)}$	Diff CH_2.	$\frac{P(M-1)}{MD}$	Diff. CH_2.
Isobutyl formate.....	45.64	....	27.70	....	32.82	....
Ethyl isobutyrate....	51.75	6.11	31.47	3.77	37.29	4.47
Methyl butyrate.....	44.17	....	26.87	....	31.80	....
Ethyl butyrate.....	51.50	7.33	30.30	4.43	36.89	5.09
Methyl isobutyrate..	44.04	....	26.58	....	31.82	....
Ethyl isobutyrate....	51.75	7.71	31.47	4.89	37.29	5.47
Methyl acetate.....	29.53	....	18.09	....	21.69	....
Ethyl "	36.44	6.81	22.24	4.15	26.47	4.78
Methyl propionate...	35.94	....	21.92	....	26.09	....
Ethyl " ...	44.01	8.67	26.57	4.65	31.79	5.70
Methyl valerate.....	51.97	....	31.60	....	37.26	....
Ethyl valerate.....	59.54	7.57	36.15	4.55	42.61	5.35
Methyl iodide.....	33.30	....	19.41	....	21.77	....
Ethyl "	41.46	8.16	24.30	4.89	27.40	5.63
Formic acid.....	14.02	....	8.57	....	10.22	....
Acetic "	21.26	7.24	12.98	4.41	15.49	5.27
Methyl alcohol.....	13.27	....	8.14	....	9.94	....
Ethyl "	21.09	7.82	12.94	4.78	15.49	5.55
Mean for sodium light..		7.56		4.55		5.33
Formic acid.....	13.94	....	8.53	....	10.28	....
Acetic "	21.55	7.61	12.93	4.41	15.44	5.16
Methyl alcohol.....	13.19	....	8.16	....	9.93	....
Ethyl "	20.73	7.54	12.71	4.55	15.23	5.30
Ethyl formate.....	29.23	....	17.93	....	21.53	....
Ethyl acetate.....	36.22	6.96	22.14	4.21	26.42	4.90
Methyl acetate.....	29.41	....	18.03	....	21.63	....
Ethyl "	36.22	6.81	22.14	4.11	26.42	4.79
Methyl benzoate.....	64.07	....	37.55	....	42.36	....
Ethyl "	71.76	7.69	42.20	4.65	47.80	5.44
		7.33		4.39		5.12

A careful inspection of the differences in table XII will show that we must have more evidence before accepting Conrady's " alleinstehenden Kohlenstoff " as having a different atomic-refraction value. In the last five examples, used for obtaining a value for red hydrogen light, the differences are about as much for as against Conrady's supposition, although

the average is decidedly in favor of it, for all three of the formulæ, and gives a greater difference than Conrady finds for the Lorentz-Lorenz formula.

Carbon United Ethylene-wise.

Carbon united ethylene-wise has a value for its atomic refraction very decidedly different from that found when the element is united in the ordinary way of the paraffins. Table XIII gives differences for a "double linking" in the column headed "difference for $1 =$." In the column headed "Formula" I have designated the number of "double linkings" by "$1=$" with a subscript figure which is the number assumed for that substance. In the case of furfurol, I have assumed three ethylene-unions since it was the only way to make furfurol a consistent substance for all of the formulæ. Its molecular refraction would indicate an alcohol- and an aldehyde group, and three ethylene-unions of carbon. If considered as having two aldehyde groups it is consistent for my formula but not for the others.

I have aimed to give sufficiently variable examples in this table to show the value of atomic refraction in detecting the ethylene union.

It will be noticed that in the first division of this table there are several numbers differing widely from the general average. I do not offer any explanation. It may be due to experimental errors. In the case of the Gladstone and the Lorentz-Lorenz formulæ, it will be found that by using the numbers usually given for atomic refraction for those formulæ the widely differing differences are not made any nearer to the average. The differences in the second part of the table are very close to each other and to the average for all three formulæ. These averages will be assumed as correct in the calculations which appear in the tables which follow.

Nitrogen.

Gladstone[1] states that "nitrogen has two values, 4.1 and 5.1 or thereabouts." He also states that "the lower value is that which was originally assigned to it and seems to be gen-

[1] J. Chem. Soc., 48, 257.

TABLE XIII.

Substance.	Formula.	Mol. wt.	Temp.	Sp. gr at t°/4°	Ind. refr. Na-light.	$\frac{P(M-1)}{D}$ Mol. refr.	Mol. refr. cal'd.	Diff. I =	$\frac{P(M^2-1)}{(M^2+2)D}$ Mol. refr.	Mol. refr. cal'd.	Diff. I =	$\frac{P(M-1)}{MD}$ Mol. refr.	Mol. refr. cal'd.	Diff. I =	Data of
Amylene	C_5H_{10} I=	70.0	20.0°	0.6476	1.3758	40.62	38.40	2.22	24.79	23.05	1.74	29.38	26.45	2.93	Brühl.
Allyl alcohol	C_3H_6O I=	58.0	"	0.8540	1.4135	28.08	25.74	2.34	16.95	15.29	1.66	19.87	17.46	2.41	"
Allyl acetate	$C_5H_8O_2$ I=	100.0	"	0.9276	1.4045	43.61	41.35	2.26	26.69	24.70	1.99	31.05	28.69	2.36	"
Allylacetic acid	"	"	7.5°	0.9903	1.4341	43.83	41.35	2.48	26.39	24.70	1.69	30.56	28.14	2.42	Gladstone.
Methyl acrylate	$C_4H_6O_2$ I=	86.0	20.0°	0.9600	1.3984	35.69	33.67	2.02	21.64	20.09	1.55	25.52	22.85	2.13	Kahlbaum.
Methyl maleate	$C_5H_8O_4$ I=	144.0	"	1.1517	1.4415	55.20	52.98	2.22	33.05	30.96	2.09	38.29	36.25	2.04	Knopps.
Ethyl crotonate	$C_6H_{10}O_2$ I=	114.0	"	0.9198	1.4245	52.61	49.05	3.56	31.66	29.31	2.35	36.93	33.98	2.41	Brühl.
Acrolein	C_3H_4O I=	56.0	"	0.8410	1.3998	26.62	23.29	3.33	16.13	14.02	2.11	19.02	15.97	3.05	Gladstone.
Mesityl oxide	$C_6H_{10}O$ I=$_2$	98.0	"	0.8578	1.4440	50.72	45.78	2.47	30.34	26.96	1.69	35.13	30.05	2.54	Brühl.
Furfurol	$C_5H_4O_2$ I=$_3$	96.0	"	1.1594	1.5261	43.56	35.35	2.74	25.41	20.38	1.77	28.54	21.58	2.31	"
Heptidene	C_7H_{12} I=$_2$	"	"	0.7458	1.4207	54.15	50.76	1.69	32.61	30.11	1.25	38.12	33.75	2.18	"
Octylene	C_8H_{16} I=	112.0	"	0.7197	1.4132	64.30	61.44	2.86	38.82	36.88	1.94	45.49	42.12	3.37	"
Valerylene	C_4H_6 I=$_2$	82.0	"	0.6786	1.4004	48.39	43.08	2 66	29.32	25.50	1.91	34.52	28.46	3.01	"
							Mean	2.53		Mean	1.82		Mean	2.55	
Benzene	C_6H_6 I=$_3$	78.0	10.0°	0.8903	1.5078	44.48	37.08	2.47	26.11	21.18	1.64	29.50	21.90	2.53	Gladstone.
"	"	"	20.0°	0.8799	1.5014	44.44	37.08	2.45	26 14	21.18	1.65	29.60	21.90	2.56	Brühl.
Toluene	C_7H_8 I=$_3$	92.0	7.5°	0.8704	1.4982	52.76	44.76	2.67	30.99	25.79	1.73	35.22	27.19	2.68	Gladstone.
"	"	"	20.0°	0.8656	1.4955	52.66	44.76	2.63	31.05	25.79	1.75	35.21	27.19	2.67	Brühl.
O-Xylene	C_8H_{10} I=$_3$	106.0	18.0°	0.8632	1.4966	60.98	52.44	2.85	35.90	30.40	1.83	40.75	32.48	2.76	Gladstone.
M-Xylene	C_8H_{10} I=$_3$	"	15.5°	0.8726	1.5020	60.38	52.44	2.85	35.55	30.40	1.81	40.60	32.48	2.71	"
P-Xylene	C_8H_{10} I=$_3$	"	16.0°	0.8488	1.4846	60.52	52.44	2.69	35.75	30.40	1.78	40.76	32.48	2.76	"
Ethylbenzene	C_8H_{10} I=$_3$	106.0	20.0°	0.8673	1.4959	60.61	52.44	2.72	35.74	30.40	1.78	40.52	32.48	2.68	Landolt.
Mesitylene	C_9H_{12} I=$_3$	120 0	"	0.8558	1.4912	68.87	60.12	2.92	40.60	35.01	1.86	46.19	37 77	2.81	Brühl.
Cumene	C_9H_{12} I=$_3$	"	12.0°	0.8432	1.4801	68.33	60.12	2.74	40.43	35.01	1.81	46.16	37.77	2.80	Gladstone.
Cymene	$C_{10}H_{14}$ I=$_3$	134.0	22.6°	0.8530	1.4847	76.14	67.80	2.78	45.00	39.62	1.79	51.28	43.06	2.74	"
Naphthalene	$C_{10}H_8$ I=$_5$	128.0	98.4°	0.9621	1.5823	77.47	58.80	3.11	44.42	33.14	1.88	48.96	33.22	2.62	Nasini.
Dimethylnaphthalene	$C_{12}H_{12}$ I=$_5$	156 0	16.4°	1.0180	1.6157	94.45	74.16	3.73	53.52	42.36	1.86	58.39	43.80	2.43	"
Phenol	C_6H_6O I=$_3$	94.0	21.0°	1.0598	1.5509	48.86	39.78	3.03	28.25	22.52	1.92	31.49	23.49	2.67	Gladstone.
Cresol	C_7H_8O I=$_3$	108.0	23.0°	1.0390	1.5419	56.32	47.46	2.95	32.46	27.13	1.78	36.53	28.78	2.58	"
M-Cresol	C_7H_8O I=$_3$	"	19.0°	1.0330	1.5364	56.08	47.46	2.87	32.63	27.13	1.83	36.50	28.78	2.57	"
α-Naphthol	$C_{10}H_8O$ I=$_5$	144.0	98.7°	1.0954	1.6206	81.58	61.50	3.34	46.21	34.50	1.95	50.33	34.81	2.59	Nasini.
Methyl benzoate	$C_8H_8O_2$ I=$_3$	136.0	20.0°	1.0862	1.5169	64.72	55.39	3.11	37.86	32.05	1.93	42.66	34.17	2.65	Landolt.
Benzyl isobutyrate	$C_{11}H_{14}O_2$ I=$_3$	178.0	23.0°	1.0058	1.4910	86.88	78.45	2.81	51.21	45.88	1.78	58.03	50.04	2.67	Gladstone.
							Mean	2.88		Mean	1.81		Mean	2.66	

erally confirmed by the nitrites of table III," and that "the higher value is where nitrogen exists in organic bases and amides." In a list of values which he gives to prove 5.1 to be an approximate value for nitrogen are given those for aniline and xylidine which are 6.39 and 6.15, respectively, instead of 5.1. This discrepancy Gladstone explains as due to the great depression of aniline and xylidine.

Table XIV has been made with the above statements of Gladstone as a basis. It will be noticed that the numbers for the bases are in the majority of cases very close to those found for the nitrites. The general average of the values for nitrogen in the bases is higher than that for the nitrites, in part on account of some abnormally high values such as those for methyldiphenylamine.

If the two very high numbers for methyldiphenylamine be rejected in the case of the Gladstone formula, the average for the bases is 5.40 instead of 5.80, as shown in the table. It will be noticed that in the case of the other two formulæ the average numbers for the nitrites are higher in both cases than the average numbers for nitrogen in the bases. If the first division of table XIV be separated into groups showing the difference for nitrogen when the nitrogen belongs to one of the three groups $-NH_2$, $=NH$, $\equiv N$, where the horizontal lines represent the number of unions with carbon—a union such as that of pyridine being counted as three—we find the following averages for the nitrogen for the three formulæ in the usual order.

For the group $-NH_2$:

Formula	$\frac{P(M-1)}{D}$	$\frac{P(M^2-1)}{(M^2+2)D}$	$\frac{P(M-1)}{MD}$
Difference for N	4.46	2.39	2.28
" "	4.40	2.31	2.08
" "	3.74	2.05	1.77
" "	3.98	2.16	1.83
" "	6.12	2.89	2.08
" "	6.48	2.99	2.11
" "	5.91	2.64	1.74
Mean.....	5.01	2.49	1.99

Table XIV.

Substance.	Formula.	Mol. wt.	Temp.	Sp. gr. at t°/4°	Ind. refr. Na light.	$\frac{P(M-1)}{D}$ Mol. refrac. Found.	Calc'd —N	Diff. N	$\frac{P(M^2-1)}{(M^2+2)D}$ Mol. refrac. Found.	Calc'd —N	Diff. N	$\frac{P(M-1)}{MD}$ Mol. refrac. Found.	Calc'd —N	Diff.	Data of
Diethyl amine	$C_4H_{11}N$	73.0	19.0°	0.7092	1.3871	39.84	35.22	4.62	24.24	21.68	2.56	28.72	26.08	2.64	Gladstone.
Triethyl "	$C_6H_{15}N$	101.0	"	0.7317	1.4005	55.28	50.58	4.70	33.49	30.90	2.59	39.47	36.66	2.81	"
Propyl "	C_3H_9N	59.0	23.5°	0.7140	1.3873	32.00	27.54	4.46	19.46	17.07	2.39	23.07	20.79	2.28	"
" "	"	"	6.5°	0.7329	1.3968	31.94	27.54	4.40	19.38	17.07	2.31	22.81	20.79	2.08	"
Dipropyl "	$C_6H_{15}N$	101.0	23.2°	0.7356	1.4025	55.27	50.58	4.69	33.46	30.90	2.56	39.42	36.66	2.76	"
" "	C_6H_{21}	143.0	22.8°	0.7535	1.4171	80.15	73.62	6.53	44.71	44.73	2.98	56.56	52.53	4.03	"
Tri propyl "	"	"	4.4°	0.7703	1.4248	78.86	73.62	5.24	47.45	44.73	2.72	55.19	52.53	2.66	"
Allyl "	C_3H_7N I=	57.0	19.0°	0.7684	1.4200	31.16	27.42	3.74	18.77	16.72	2.05	21.94	20.17	1.77	"
" "	"	"	10.5°	0.7754	1.4272	31.40	27.42	3.98	18.88	16.72	2.16	22.00	20.17	1.83	"
Methyldiphenyl amine	$C_{13}H_{13}N$ I=$_6$	183.0	20.0°	1.0476	1.6193	108.17	97.62	10.55	61.31	56.75	4.56	66.80	63.41	3.39	Brühl.
" "	"	"	24.6°	1.0466	1.6166	107.81	97.62	10.19	61.14	56.75	4.39	66.70	63.41	3.29	Gladstone.
Pyrroline	C_4H_7N I=	69.0		0.9606	1.5074	36.45	32.10	4.35	21.39	19.17	2.22	24.17	22.18	1.99	"
Aniline	C_6H_7N I=$_3$	93.0	13.0°	1.0160	1.5828	53.34	47.22	6.12	30.58	27.69	2.89	33.70	31.62	2.08	"
Toluidine	C_7H_9N I=$_3$	107.0	20.0°	0.9986	1.5728	61.38	54.90	6.48	35.29	32.30	2.99	39.02	36.91	2.11	Brühl.
Xylidine	$C_8H_{11}N$ I=$_3$	121.0	19.0°	1.9867	1.5585	68.49	62.58	5.91	39.55	36.91	2.64	43.94	42.20	1.74	Gladstone.
Dimethyaniline	"	"	20.0°	0.9575	1.5587	70.60	62.58	8.02	40.79	36.91	3.88	45.29	42.20	3.09	Brühl.
Benzylaniline	$C_{13}H_{13}N$ I=$_6$	183.0	24.8°	1.0619	1.6113	105.43	97.62	7.81	59.88	55.75	4.13	65.41	63.41	2.00	Gladstone.
Pyridine	C_5H_5N I=$_3$	79.0	20.0°	0.9792	1.5088	41.05	36.66	4.39	24.08	21.27	2.81	27.11	23.67	3.54	Berliner.
Picoline	C_6H_7N I=$_3$	93.0	"	0.9469	1.5026	48.58	44.34	4.24	29.01	25.88	3.13	32.33	28.86	3.49	"
"	"	"	23.5°	0.9409	1.5006	49.48	44.34	5.14	29.09	25.88	3.21	32.97	28.86	4.11	Gladstone.
Piperidine	$C_5H_{11}N$ I=$_6$	85.0	20.0°	0.8622	1.4449	43.86	39.90	3.96	26.23	24.13	2.10	30.35	28.09	2.26	Berliner.
Quinoline	C_9H_7N I=$_5$	129.0	"	1.0947	1.6171	72.72	67.02	5.70	41.23	38.66	2.57	44.96	42.87	2.09	"
"	"	"	"	1.1021	1.6330	74.10	67.02	7.08	41.80	38.66	3.14	45.37	42.87	2.50	Gladstone.
"	"	"	18.0°	1.0960	1.6282	73.94	67.02	6.92	41.78	38.66	3.12	45.41	42.87	2.54	"
							Mean	5.80			2.92			2.63	
Propionitrile	C_3H_5N	55.0	19.0°	0.7862	1.3681	25.75	21.54	4.21	15.76	12.75	3.01	18.92	14.23	4.69	Gladstone.
Valeronitrile	C_5H_9N	83.0	18.0°	0.8010	1.3917	40.59	36.92	3.67	24.65	21.97	2.68	29.16	24.81	4.35	"
Capronitrile	$C_6H_{11}N$	97.0	"	0.8040	1.4087	49.31	44.60	4.71	29.81	26.58	3.23	35.00	30.10	4.90	"
Benzonitrile	C_7H_5N I=$_3$	103.0	"	1.0052	1.5306	54.36	48.90	5.46	31.67	27.98	3.69	35.52	30.35	5.17	"
"	"	"	20.0°	1.0076	1.5289	54.06	48.90	5.16	31.52	27.98	3.54	35.36	30.35	5.01	Berliner.
Trimethylene cyanide	$C_5H_6N_2$	94.0	23.2°	0.9888	1.4365	41.49	32.40	4.56	24.87	18.73	3.07	28.88	19.89	4.60	
							Mean	4.63			3.20			4.79	

For the group =NH :

	Formula $\frac{P(M-1)}{D}$	$\frac{P(M^2-1)}{(M^2+2)D}$	$\frac{P(M-1)}{MD}$
Difference for N	4.62	2.56	2.64
" "	4.69	2.56	2.76
" "	4.35	2.22	1.99
" "	7.81	4.13	2.00
" "	3.96	2.10	2.26
Mean.....	5.09	2.71	2.35

For the group ≡N:

	Formula $\frac{P(M-1)}{D}$	$\frac{P(M^2-1)}{(M^2+2)D}$	$\frac{P(M-1)}{MD}$
Difference for N	4.70	2.59	2.81
" "	6.53	2.98	4.03
" "	5.24	2.72	2.66
" "	10.55	4.56	3.39
" "	10.19	4.39	3.29
" "	8.02	3.88	3.09
" "	4.39	2.81	3.54
" "	4.24	3.13	3.49
" "	5.14	3.21	4.11
" "	5.70	2.57	2.09
" "	7.08	3.14	2.50
" "	6.92	3.12	2.54
Mean.....	6.56	3.26	3.13

If, in the second group, 7.81 be taken from the first column and 4.13 from the second, both averages would be smaller than found in group $-NH_2$ for the corresponding formulæ.

If, from the first column of the third group, the numbers 10.55, 10.19, and 8.02 be rejected, the average is still 5.54; therefore, all three formulæ show higher numbers for the group ≡N than for either of the other groups. We may sum up the result of the grouping as follows:

	Formula $\frac{P(M-1)}{D}$	$\frac{P(M^2-1)}{(M^2+2)D}$	$\frac{P(M-1)}{MD}$
Difference for N in the group $-NH_2$.....	5.01	2.49	1.99
Difference for N in the group =NH	5.09	2.71	2.35
Difference for N in the group ≡N.....	5.54	3.26	3.13
Difference for N in cyanides,	4.63	3.20	4.79

It will be noticed that there is a gradual increase in the numbers for the formula $\frac{P(M-1)}{MD}$ from group $-NH_2$ to group $\equiv NH$, which would indicate that the union with carbon gave greater numbers for nitrogen than that with hydrogen. The large differences for nitrogen accounted for, by Gladstone, by their great dispersion are easily accounted for in the formula $\frac{P(M-1)}{MD}$ by the number of unions with carbon. While the numbers for the first two groups are too close together to be of much practical value, the numbers for groups 3 and 4 are far enough from each other and from groups 1 and 2 to be of value in determining whether nitrogen has three unions with carbon or is nitrogen of a cyanide. This is not true of the other two formulæ.

Chlorine, Bromine, and Iodine.

Since the values found in this paper for CH_2 so nearly agree with the values found by others for CH_2 when either the Gladstone or the Lorentz-Lorenz formula was used, it might be expected that the values for the halogens would not differ much from those found by others. Gladstone has found for his formula: 9.9 for chlorine; 15.3 for bromine; and 24.5 for iodine. Haagen, using the same formula, found 9.8 for chlorine; 15.3 for bromine; and 24.8 for iodine. For the same formula I find—notwithstanding the different values for carbon and hydrogen—10.11 for chlorine; 15.32 for bromine; and 25.09 for iodine. The numbers found by Haagen and Gladstone were for red hydrogen light while those found in this paper are for sodium light. Conrady, using numbers for sodium light found 5.998 for chlorine, 8.927 for bromine; and 14.12 for iodine, for the Lorentz-Lorenz formula, while in this paper I have found 6.03 for chlorine; 8.84 for bromine; and 14.01 for iodine. These numbers agree also very closely with those found by Brühl for red hydrogen light: 6.02 for chlorine; 8.95 for bromine; and 13.99 for iodine.

For the formula $\frac{P(M-1)}{MD}$ the numbers found in this paper are 7.20 for chlorine; 9.95 for bromine; and 15.32 for iodine.[1]

[1] See tables XV, XVI, and XVII for the method of determining these numbers.

TABLE XV.—*Chlorine Derivatives.*

Substance.	Formula.	Mol. wt.	Temp.	Sp. gr. at t°/4°	Ind. refr. Na light.	$\frac{P(M-1)}{D}$ Found	$\frac{P(M-1)}{D}$ Calc'd — Cl.	$\frac{P(M-1)}{D}$ Diff. for Cl.	$\frac{P(M^2-1)}{(M^2+2)D}$ Found.	$\frac{P(M^2-1)}{(M^2+2)D}$ Calc'd — Cl.	$\frac{P(M^2-1)}{(M^2+2)D}$ Diff. for Cl.	$\frac{P(M-1)}{MD}$ Found.	$\frac{P(M-1)}{MD}$ Calc'd — Cl.	$\frac{P(M-1)}{MD}$ Diff. for Cl.	Data of
Propyl chloride	C_3H_7Cl	78.5	20.0°	0.8898	1.3886	34.28	24.54	9.74	20.84	14.91	5.93	24.69	17.51	7.18	Brühl.
Isobutyl "	C_4H_9Cl	92.5	19.0°	0.8626	1.3979	42.67	32.22	10.45	25.87	19.52	6.35	30.52	22.80	7.72	Gladstone.
Amyl "	$C_5H_{11}Cl$	106.5	20.0°	0.8740	1.4102	49.98	39.90	10.08	30.17	24.13	6.04	35.44	28.09	7.35	Jahn.
Ethylene	$C_2H_4Cl_2$	99.0	"	1.2501	1.4444	35.19	15.36	9.92	21.05	9.22	5.92	24.36	10.58	6.89	Weegmann.
Ethylidine "	"	"	"	1.1750	1.4168	35.16	15.36	9.99	27.15	9.22	5.98	24.78	10.58	7.10	"
Allyl "	C_3H_5Cl I =$_1$	76.5	"	0.9379	1.4154	33.91	24.42	9.49	20.44	14.56	5.88	23.96	16.89	7.07	Brühl.
Butyryl "	C_4H_7ClO	106.5	"	1.0277	1.4121	42.71	32.47	10.24	25.75	19.71	6.07	30.24	22.90	7.34	"
Acetyl "	C_2H_3ClO	78.5	"	1.1051	1.3898	27.69	17.11	10.58	16.83	10.49	6.34	19.92	12.32	7.60	"
Chloral	C_2HOCl_3	147.5	"	1.5121	1.4557	44.46	14.11	10.12	26.49	8.33	6.05	30.54	9.04	7.17	"
Chloroform	$CHCl_3$	119.5	"	1.4898	1.4467	35.84	6.18	9.89	21.41	3.53	5.96	24.77	3.65	7.04	Haagen.
Ethyl dichloracetate	$C_4H_6Cl_2O_2$	157.0	"	1.4821	1.4386	53.71	33.67	10.02	32.17	20.09	6.04	37.33	22.85	7.24	Brühl.
Ethyl trichloracetate	$C_4H_5Cl_3O_2$	191.5	"	1.3826	1.4507	62.41	32.17	10.08	37.27	19.01	6.08	43.02	21.21	7.27	"
Monochlorbenzene	C_6H_5Cl I =$_3$	112.5	"	1.1066	1.5248	53.35	44.22	9.13	31.14	25.53	5.61	34.99	28.24	6.75	"
"	"	"	22.5°	1.1047	1.5232	53.28	44.22	9.06	31.12	25.53	5.59	34.98	28.24	6.74	Gladstone.
Monochlortoluene	C_7H_7Cl I =$_3$	126.5	19.0°	1.0761	1.5271	61.96	51.90	10.06	36.14	30.14	6.00	40.57	33.53	7.04	"
Benzyl chloride	"	"	7.0°	1.0990	1.5415	61.93	51.90	10.03	36.19	30.14	6.04	40.17	33.53	6.64	"
Benzoyl chloride	C_7H_5ClO I =$_3$	140.5	20.0°	1.2122	1.5537	64.18	52.15	12.03	37.12	30.33	6.79	41.31	33.63	7.68	Brühl.
Tetrahydronaphthalene dichloride	$C_{10}H_8Cl_2$ I =$_6$	199.0	18.0°	1.2648	1.6247	98.29	76.08	11.10	35.60	44.00	5.80	64.49	49.18	7.65	Ketteller.
							Mean	10.11			6.03			7.20	

TABLE XVI.—*Bromine Derivatives.*

Substance.	Formula.	Mol. wt.	Temp.	Sp. gr at t°/4°	Ind. refr. Na-light.	$\frac{P(M-1)}{D}$ Found.	Calc'd — Br.	Diff. for Br.	$\frac{P(M^2-1)}{(M^2+2)D}$ Found.	Calc'd — Br.	Diff. for Br.	$\frac{P(M-1)}{MD}$ Found.	Calc'd — Br.	Diff. for Br.	Data of
Ethyl bromide.....	C_2H_5Br	109.0	20.0°	1.4555	1.4239	31.74	16.86	14.88	19.48	10.30	9.18	22.29	12.22	10.09	Weegmann.
" "		"	"	1.4569	1.4241	31.73	16.86	14.87	19.10	10.30	8.80	22.28	12.22	10.08	Haagen.
Propyl "	C_3H_7Br	123.0	"	1.3520	1.4339	39.47	24.54	14.93	23.68	14.91	8.77	27.53	17.51	10.02	Brühl.
Isopropyl "	"	"	"	1.3097	1.4251	39.93	24.54	15.39	24.02	14.91	9.11	28.01	17.51	10.50	"
Amyl "	$C_5H_{11}Br$	151.0	"	1.2202	1.4412	55.42	39.90	15.52	33.17	24.13	9.04	38.45	28.09	10.36	Haagen.
Allyl "	C_3H_5Br $1=_1$	121.0	"	1.3980	1.4655	40.29	24.42	15.87	23.74	14.56	9.18	27.43	16.89	10.54	Brühl.
Acetylene dibromide.....	$C_2H_2Br_2$ $1=_1$	186.0	"	2.2289	1.5437	45.37	15.24	15.07	26.32	8.87	8.73	29.39	9.96	9.72	Weegmann.
Acetylene tetrabromide..	$C_2H_2Br_4$	346.0	"	2.9673	1.6380	74.39	12.36	15.51	41.90	7.06	8.71	45.42	7.30	9.53	"
Ethylene bromide.....	$C_2H_4Br_2$	188.0	"	2.1768	1.5379	46.45	15.36	15.55	27.00	9.22	8.89	30.21	10.58	9.82	"
Ethylidine "		"	"	2.0555	1.5128	46.01	15.36	15.75	27.47	9.22	9.13	31.01	10.58	10.22	"
Amyline "	$C_5H_{10}Br_2$	230.0	21.0°	1.6560	1.5076	70.50	38.40	16.05	41.35	24.56	8.40	46.76	26.45	10.16	Gladstone.
Bromoform	$CHBr_3$	253.0	20.0°	2.8189	1.5899	52.85	6.18	15.56	30.23	3.53	8.90	33.26	3.65	9.87	Jahn.
Brombenzene.....	C_6H_5Br $1=_3$	157.0	"	1.4914	1.5598	58.92	44.22	14.70	34.02	25.53	8.49	37.37	28.24	9.13	Brühl.
"	"		23.5°	1.4925	1.5577	58.66	44.22	14.44	33.88	25.52	8.35	37.65	28.24	9.41	Gladstone.
Bromtoluene.....	C_7H_7Br $1=_3$	171.0	"	1.4192	1.5608	67.56	51.90	15.66	39.01	30.14	8.87	43.29	33.53	9.76	"
a-Bromnaphthalene	$C_{10}H_7Br$ $1=_6$	207.0	25.2°	1.4847	1.6565	91.54	74.58	16.96	51.25	42.92	8.33	55.26	47.54	7.72	Kanonnikoff.
"	"	"	16.5°	1.4888	1.6601	91.78	74.58	17.20	51.32	42.92	8.40	55.23	47.54	7.69	Nasini.
β-Bromnaphthalene.....	"	"	"	1.5678	1.6669	88.06	74.58	13.48	49.12	42.92	6.20	52.83	47.54	5.29	Gladstone.
"	"	"	18.0°	1.5403	1.6630	89.09	74.58	14.51	49.78	42.92	6.86	54.17	47.54	6.63	"
	Mean with the bromnaphthalene rejected							15.32			8.84			9.95	

TABLE XVII.—*Iodine Derivatives.*

Substance.	Formula.	Mol. wt.	Temp.	Sp. gr. at t°/4°	Ind. of refr. for Na-light.	$\frac{P(M-1)}{D}$ Found.	$\frac{P(M-1)}{D}$ Calc'd —I.	$\frac{P(M-1)}{D}$ Diff. for I.	$\frac{P(M^2-1)}{(M^2+2)D}$ Found.	$\frac{P(M^2-1)}{(M^2+2)D}$ Calc'd —I.	$\frac{P(M^2-1)}{(M^2+2)D}$ Diff. for I.	$\frac{P(M-1)}{MD}$ Found.	$\frac{P(M-1)}{MD}$ Calc'd —I.	$\frac{P(M-1)}{MD}$ Diff. for I.	Data of
Methyl iodide	CH_3I	142.0	20.0°	2.2582	1.5297	33.30	9.18	24.12	19.41	5.69	13.72	21.77	6.93	14.84	Haagen.
" "	"	"	21.0°	2.2740	1.5293	33.04	9.18	23.86	19.26	5.69	13.57	21.61	6.93	14.68	Gladstone.
Ethyl "	C_2H_5I	156.0	20.0°	1.9305	1.5731	41.46	16.86	24.60	24.30	10.30	14.00	27.40	12.22	15.18	Haagen.
Propyl "	C_3H_7I	170.0	"	1.7427	1.5051	49.16	24.54	24.62	28.93	14.91	14.02	32.66	17.51	15.15	Brühl.
Isopropyl "	"	"	"	1.7033	1.4997	49.86	24.54	25.32	29.34	14.91	14.43	33.25	17.51	15.74	"
Butyl "	C_4H_9I	184.0	"	1.6166	1.5001	56.91	32.22	24.69	33.47	19.52	13.95	37.94	22.80	15.14	"
Isobutyl "	"	"	"	1.6056	1.4960	56.78	32.22	24.56	33.47	19.52	13.95	37.99	22.80	15.19	"
Isoamyl "	$C_5H_{11}I$	198.0	14.0°	1.5048	1.4960	65.26	39.90	25.36	38.43	24.13	14.30	43.62	28.09	15.53	Gladstone.
Sec-amyl "	"	"	20.0°	1.4703	1.4908	66.09	39.90	26.19	38.93	24.13	14.80	45.00	28.09	16.91	Haagen.
Sec-hexyl "	$C_6H_{13}I$	212.0		1.4193	1.4948	73.90	47.58	26.32	43.52	28.74	14.78	49.44	33.38	16.06	Gladstone.
Methylene diiodide	CH_2I_2	268.0	19.0°	3.3188	1.7421	59.95	7.68	26.14	32.64	4.61	14.02	34.41	5.29	14.56	"
Trimethylene iodide	$C_3H_6I_2$	296.0	7.5°	2.5890	1.6479	74.06	23.04	25.52	41.59	13.71	13.94	44.94	15.87	14.54	"
Iodobenzene	C_6H_5I	192.0	22.2°	1.8300	1.6197	69.07	44.22	24.85	39.13	25.53	13.60	42.65	28.34	14.31	"
							Mean	25.09			14.01			15.22	

Sulphur.

Divalent sulphur, like oxygen, has two very different values for its atomic refraction: one when its union corresponds to hydroxyl- or ether-oxygen, and another when its union corresponds to carbonyl oxygen. As in the case of oxygen the second value is the higher and enough higher to be of value in determining the kind of union with carbon. This would indicate that the kind of union is much the same for sulphur and oxygen whatever the union may be. Table XVIII will show these different values and the method of obtaining them.

Carbon disulphide has been calculated as having one carbonyl sulphur and one ether-sulphur. Ethyl sulphocarbonate and ethyl dithiosulphocarbonate illustrate the influence of the dispersive power of sulphur on the numbers obtained for sulphur. For the Gladstone and Lorentz-Lorenz formulæ, the first gives a number about as much below as the second does above the mean. The mean corresponds to the numbers obtained from the substances having two atoms of sulphur in the molecule. The formula $\frac{P(M-1)}{MD}$ would indicate that carbon disulphide is not truly represented by a carbonyl sulphur atom and an ether-sulphur atom.

E. Wiedemann,[1] found that for the Gladstone formula the numbers for sulphur were greater the greater the proportion of sulphur in the substance. He also found for the Lorentz-Lorenz formula two values for sulphur: 7.93 for sulphur of sulphides and hydrosulphides (hydroxyl or ether-unions), and 9.29 for carbonyl unions.

In conclusion I give the following comparative table. The numbers in column I are those given by Gladstone[2] for ray A, and are the same as those given by Landolt and others for ray Hα(C). In column II are given Landolt's numbers[3] for ray A. The numbers found in this paper for ray Hα are given in column III, and for ray Nα(D) are given in column IV. Column V contains Landolt's numbers[3] for ray A. Brühl's

[1] Ann. der phys. Wied., **17**, 577, (1882).
[2] J. Chem. Soc., **45**, 244, (1884).
[3] Ann. Chem. (Liebig), **213**, 112 (1882).

TABLE XVIII.

Substance.	Formula.	Mol. wt.	Temp.	Sp. gr. at t°/4°	Ind. refr. for Na—light.	$\frac{P(M-1)}{D}$ Found.	Calc'd —S.	Diff. for S.	$\frac{P(M^2-1)}{(M^2+2)D}$ Found.	Calc'd —S.	Diff. for S.	$\frac{P(M-1)}{MD}$ Found.	Calc'd —S.	Diff. for S.	Data of
Ethyl mercaptan	C_2H_6S	62.0	20.0°	0.8931	1.4306	29.89	18.36	11.53	17.96	11.38	6.58	20.89	13.86	7.03	Nasini.
Isobutyl "	$C_4H_{10}S$	90.0	"	0.8357	1.4386	47.23	33.72	13.51	28.30	20.60	7.70	32.76	24.44	8.32	"
Isoamyl "	$C_5H_{12}S$	104.0	"	0.8348	1.4412	54.96	41.40	13.56	32.91	25.21	7.70	38.38	29.73	8.65	"
Ethyl sulphide	$C_4H_{10}S$	90.0	"	0.8368	1.4423	47.57	33.72	13.85	28.47	20.60	7.87	32.98	24.44	8.54	"
Amyl "	$C_{10}H_{22}S$	174.0	"	0.8431	1.4524	93.37	79.80	13.57	55.71	48.26	7.45	64.28	56.18	8.10	"
Allyl "	$C_6H_{10}S$ 1=1	114.0	26.8°	0.8877	1.4877	62.64	48.84	13.80	36.97	29.12	7.85	42.11	33.78	8.33	"
" "	" 1=1	"	"	0.8544	1.4598	61.34	48.84	12.50	36.53	29.12	7.41	42.02	33.78	8.24	Gladstone.
Thiophene	C_4H_4S 1=1	84.0	25.1°	1.0593	1.5268	41.77	30.48	11.29	24.37	17.74	6.63	27.36	19.92	7.44	Nasini.
"	"	84.0	20.0°	1.0643	1.5285	41.71	30.48	11.29	24.32	17.74	6.58	27.29	19.92	7.37	Knops.
Mean, with the first one and last two rejected..								13.47			7.66			8.36	
Ethylpropyl xanthate	$C_6H_{12}S_2O$	164.0	26.5°	1.0505	1.5264	82.18	62.25	19.93	47.94	36.78	11.16	53.84	41.69	12.15	Nasini.
Methylpropyl "	$C_5H_{10}S_2O$	150.0	24.8°	1.0841	1.5355	74.08	54.57	19.51	43.10	32.17	10.93	48.25	36.40	11.85	"
Ethylethyl "	"	"	18–19°	1.0850	1.5370	74.24	54.57	19.67	43.19	32.17	11.02	48.03	36.40	11.63	Wiedemann.
Methylethyl "	$C_4H_8S_2O$	136.0	25.0°	0.1189	1.5462	66.38	46.68	19.70	38.50	27.56	10.94	42.93	31.11	11.82	Nasini.
Ethyl sulphocarbonate	$C_3H_{10}SO_2$	134.0	18–19°	1.0330	2.4501	59.68	43.80	15.88	35.54	25.97	9.57	40.88	29.63	11.25	Wiedemann.
Ethyl dithiosulphocarb'te	$C_3H_{10}S_3$	166.0	"	1.1520	1.6210	89.49	65.34	24.15	50.68	38.37	12.31	55.21	43.80	11.41	"
Carbon disulphide	CS_2	76.0	20.0°	1.2634	1.6279	37.77	18.15	19.52	21.34	10.11	11.23	23.20	10.37	12.83	Lorenz.
							Mean	19.76			11.02			11.85	

numbers[1] for ray Ha(C) are given in column VI. Column VII contains Conrady's numbers.[2] Columns VIII, IX, X, and XI contain numbers found in this paper.

	$\frac{P(M-1)}{D}$				$\frac{P(M_0-1)}{(M_0+2)D}$					$\frac{P(M-1)}{MD}$	
	I. Ray A.	II. Ray A.	III. Ray Ha.	IV. Ray Na(D).	V. Ray A.	VI. Ray Ha(C).	VII. Ray Na(D).	VIII. Ray Na(D).	IX. Ray Ha(C).	X. Ray Ha(C).	XI. Ray Na(D).
Carbon, saturated	5.0	4.86	4.61	4.68	2.43	2.48	2.501	2.45	2.33	2.00	2.01
" in Ca Hn	5.95	...	...	...	...	...	...	...	...	...	...
" double linked	6.1	5.86	...	...	...	...	...	...	...	...	...
" standing alone	...	...	...	4.68(?)	...	...	2.593	2.45(?)	...	...	2.01(?)
" double linking increment 1=	...	2.00	...	2.88	1.59	1.78	1.707	1.81	...	...	2.66
Hydrogen	1.3	1.29	1.50	1.50	1.02	1.04	1.051	1.08	1.11	1.64	1.64
Oxygen hydroxyl	2.80	2.71	2.72	2.70	1.56	1.58	1.521	1.46	1.52	1.63	1.59
" ether	...	...	...	2.70(?)	...	...	1.683	1.46(?)	...	...	2.13
" carbonyl	3.40	3.29	2.27	3.25	2.89	2.34	2.287	2.35	2.37	3.30	3.38
Nitrogen in $-NH_2$	...	...	...	5.01	...	...	...	2.49	...	...	1.99
" $=NH$	5.10	...	...	5.09	...	3.02(?)	...	2.71(?)	...	...	2.35
" $\equiv N$	...	...	...	5.54	...	...	...	3.26	...	...	3.13
" cyanides	4.10	...	...	4.63	...	...	...	3.20	...	...	4.79
Chlorine	9.9	9.53	...	10.11	5.89	6.02	5.998	6.03	...	...	7.20
Bromine	15.3	14.75	...	15.32	...	8.95	8.927	8.84	...	...	9.95
Iodine	24.5	23.55	...	25.09	...	13.99	14.12	14.01	...	...	15.22
Sulphurin place of hydroxyl oxygen	14.1	...	...	13.47	...	...	...	7.66	...	...	8.36
" " carbonyl	16.0	14.74	...	19.76	...	...	...	11.02	...	...	11.85

CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN.

[1] Ztschr. phys. Chem., 1, 306 (1887). [2] Ztschr. phys. Chem., 3, 226 (1889).

A NEW APPARATUS FOR DETERMINING MOLECULAR WEIGHTS BY THE BOILING-POINT METHOD.

By H. B. Hite.

In determining molecular weights by the boiling-point method, one of the principal sources of error is that due to changes in atmospheric pressure, errors from this source alone being quite sufficient, often, to render the results absolutely worthless. Indeed, one who has not had occasion to make accurate readings of the barometer *at short intervals* would hardly believe how great or how capricious these changes may be. The correction for such errors may be obtained from the barometer directly, or better, from a second boiling-point apparatus, but there is no apparatus that of itself makes any attempt to correct for these errors.

Two years ago, work was begun in this laboratory on an apparatus which, it was hoped, would not only be entirely independent of changes in atmospheric pressure, but tend to eliminate a number of other errors. The method was briefly as follows:

Instead of using one boiling-flask and a thermometer, it was proposed to use two flasks, each carrying in the position usually occupied by the thermometer, a tube containing one set of the terminals of a thermopile. Any difference in the temperature of the two boiling liquids, such as would be caused by the dissolution of some substance in one of them could be measured with a galvanometer; or the molecular weight of the substance could be determined from the amount of known substance that would have to be added to the other flask to bring the galvanometer to its original position. Changes in atmospheric pressure, however, would not be recorded as they would affect both liquids alike. Many advantages of such a method will suggest themselves. But there were also some disadvantages connected with it, and some of these became more apparent as the work proceeded. The Beckmann apparatus was found to be poorly adapted to such work. It is fragile, complicated, and will vary with the heat applied to it. There are other causes of variation that

are not always so easy to discover. The movements of the thermometer in response to changes in atmospheric pressure are sluggish and uncertain; indeed, the general behavior of the apparatus is not always such as would be calculated to inspire the greatest confidence in it.

In the attempt to devise a simpler and more reliable boiling-apparatus—which required a great deal more time than had been anticipated,—the galvanometer method was lost sight of. It will, however, be taken up again in the near future, a number of improvements having meanwhile suggested themselves. But as the boiling-apparatus devised for this purpose can be used to advantage in determining molecular weights with a thermometer in the usual way, it is thought well to describe it before going further.

More than a hundred forms of apparatus were carefully fitted up and thoroughly tested. A number of these would determine molecular weights with considerable accuracy. Most of them would distinguish between multiples. It will be impossible in this connection to do more than mention a few of the typical forms.

Boiling by Means of an Electric Current.—One of the first forms tried was constructed as follows:

A large test-tube which served as a boiling vessel was closed by a stopper carrying the thermometer, condenser, and a small glass tube. This tube extended to near the bottom of the test-tube, and contained two insulated copper wires, the lower ends of which were connected by a loop of platinum wire. This extended beyond the end of the tube, which was closed upon the loop in the same way that the film is arranged in an incandescent lamp. The loop was then bent at right angles to the tube so that it would lie on, or near the bottom of the test-tube. The test-tube was suspended in an air-bath which furnished the heat to boil the liquid, while the hot wire caused the liquid in contact with it to burst into bubbles at once, and these prevented the liquid from becoming superheated. The boiling was very regular, the liquid appearing like a mass of bubbles. But, if the current was increased or decreased, the thermometer would fall or rise according as the temperature of the air-bath was much above or below the

boiling-point of the liquid. This apparatus was varied in many ways, but was never quite satisfactory.

Stirring the Liquid.—The freezing-point method has a decided advantage in that the ice remains in the liquid, and by stirring may be brought in contact with every part of it; while the bubbles which play an exactly similar part in a boiling liquid pass quickly to the surface. Then, the bubbles are not distributed uniformly, but start from a few points on the bottom of the glass. There will be upward currents over these points, and the bubbles passing to the surface *with* the current come in contact with still less of the liquid.

Again, heat must be added to the boiling liquid much more rapidly than it need be withdrawn from the freezing liquid. If, in the freezing-point method, it were necessary to undercool the liquid until ice formed of its own accord, and, if the ice immediately escaped from the liquid to be melted and returned at a much higher temperature, it would be a far more difficult matter to get a constant freezing-point. If, on the other hand, in the boiling-point method, the liquid could be carefully super-heated a certain amount, a bubble dropped in to start the formation of bubbles, and if these could be stirred with the liquid until they had come in contact again and again, with every part of it, a constant boiling-point could be much more easily obtained. Hoping to approach these conditions, an apparatus was constructed as follows: A glass jar of 1½ liters capacity, containing a liter of liquid was closed by a stopper carrying a thermometer and return-flow condenser, and placed in a double-walled air-bath, between the walls of which a liquid was kept boiling at a temperature above the boiling-point of the liquid in the jar. By means of a stirrer, the handle of which passed out through the condenser, it was an easy matter, not only to stir the liquid, but to keep it filled with bubbles. This is a very imperfect description of an apparatus that was fitted up with a great deal of care. The liquid was allowed to become super-heated about 1/2 degree, and the stirring begun. The thermometer would fall, but it would continue to fall without so much as pausing at the boiling-point. The apparatus has since been greatly improved, and it is still hoped it may be made to give satisfactory results.

Thermometer in the Vapor.—The liquid in a distilling-bulb may be far from pure and yet the thermometer in the neck of the bulb will give the boiling-point of the pure liquid. The volume of vapor filling the flask is in contact with the solution only on one side, and that is far removed from the thermometer, while it is in contact on all other sides with the pure (distilled) liquid, wetting the walls, and this is at the boiling-point. If the vapor in contact with the thermometer bulb were surrounded by the solution instead of the distilled liquid it ought to give the boiling-point of the solution. In the hope of realizing these conditions, an apparatus was constructed as follows: A Schleicher and Schüll filter-thimble (Fig. 1) was closed with a piece of cork which had a hole in the middle to admit the thermometer bulb. A small piece of glass tubing T bent as shown, passed through another hole in the cork. The thermometer bulb enclosed in the thimble in this way, was submerged in the liquid. When first submerged, the bulb is surrounded by air, but this is soon displaced by the rapid evaporation from the free, wet, inner walls of the thimble. When the liquid is boiling, the vapor pours out of the tube, T, which is slightly drawn out to a point and bent to one side so that the bubbles will escape more regularly. It is to be observed that in this arrangement the thermometer bulb is in the midst of a mass of vapor, which is in contact, practically, on all sides with the boiling solution. On heating the pure liquid to boiling, the thermometer rises steadily and remains perfectly constant or follows the barometer. On adding some substance to the liquid, the thermometer rises rapidly, at first, then more and more slowly, and does not reach the correct elevation in an hour, though continually approaching it. This apparatus, like all the other simple forms mentioned, was varied in many ways, but it was never satisfactory. As an apparatus for determining the absolute boiling-point of pure liquids, it might have some advantages, as the thermometer bulb is so well protected. The trouble in the case of solutions is probably due to the condensation on the thermometer bulb.

FIGURE 1.

Balls of Platinum Gauze.—It is necessary that some part of

a liquid boiling under ordinary conditions should be heated considerably above its boiling-point, in order that bubbles may be formed. This, of course causes great irregularities in temperature. If there were always a liberal supply of bubbles remaining in the liquid, a much gentler heat would be sufficient. An apparatus constructed as follows was an attempt in this direction: A boiling-tube provided with a thermometer and condenser, arranged as usual, was placed in an air-bath, and filled to the surface of the liquid with hollow balls, 3 mm. in diameter, made of closely-woven platinum gauze. When the balls are dropped into the liquid, each encloses a bubble of air. This expands as the liquid is heated, until the pressure is sufficient to cause a part of the air to force its way out between the meshes of the gauze. The air is soon displaced by vapor. In this apparatus the boiling was very regular, and it could be used for determining molecular weights, but it is far less accurate than another apparatus that had meanwhile been devised, and for which work on all other forms was suspended, possibly before the apparatus just described had received the attention it deserved.

An Inverted Specimen Tube.—A boiling liquid is always super-heated, and the extent to which it is super-heated depends upon many circumstances, among which may be mentioned the character of the surface of the flask. A small rough place will serve as a starting-point for a stream of bubbles which will of course lower the temperature in that part of the flask. But specks and rough places in the glass can never be depended upon. They are liable to become inactive at any time. To promote regular boiling, Beckmann introduced what has been the characteristic feature of his apparatus ever since,—a platinum wire sealed in the bottom of the flask. Gernhardt states[1] that the bubbles do not start from the wire, but from the fusible glass used in fixing the wire. It is probable that the bubbles start from some small cracks or crevices around the wire or between the fusible glass and the flask. Instead of the platinum wire or the fusible glass, or both, the author would suggest the use of a small specimen tube, placed in the boiling tube, so that the open end rests on the bottom, and the closed end against the side of the boiling-tube. The lower

[1] Ber. d. chem. Ges., **27**, 964.

part of the boiling-tube should be filled with beads as usual. There will always be a bubble at the end of the specimen-tube where the heat is being applied.

Boiling by Means of the Vapor.—Since a salt-solution may be heated far above the boiling-point of the pure solvent by passing its vapor through it, it seemed not improbable that, if the solution were carefully jacketed, and the vapor came directly from a salt-solution of the same concentration, an accurate boiling-point might be obtained in this way. At all events, it seemed highly improbable that the solution would be super-heated, and, as it was suspected that most of the difficulties with other forms of apparatus were due to super-heating the liquid, it was determined to give this idea a thorough trial. The first attempt was entirely satisfactory. The thermometer following the barometer for two days and the greater part of a night almost as closely as the two instruments could be read. Fig. 2 shows one of the first forms used. It is a vertical section through the boiling flask and adjoining parts reduced one-half. A boiling-flask, F, is closed by a stopper S, which is ground into the neck N. This stopper opens into the condenser K, and the tube T is suspended from it. The lower, wider part of this tube, is jacketed by the tube J. The tubes are blown together as shown at *b*. The lower end of the tube T is closed by a cup-shaped stopper C, the bottom of which is drawn out into a short tube *t*, which has a hole, *h*, in the side, through which the liquid in the flask may mix with that in the tube T. The stopper C has three or four small notches *n*–*n*, cut vertically across its ground surface with the sharp corner of a wet file. When the stopper is in position, these notches form so many small holes through which the vapor collected in the lower part of the jacket,—the space V,—may stream up into the liquid in the tube T. A hole H, allows it to pass out into the stopper S, and

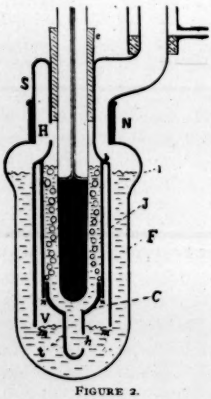


FIGURE 2.

into the condenser with the vapor from the flask. The condensed vapor is all returned to the flask. A thin cork stopper *c*, holds the thermometer in place. The flask is filled with liquid to the line *l–l*, and when boiling the vapor displaces the liquid from the jacket so that there is a free surface as indicated by the line *m–m*. The bottom of the flask is filled with balls of platinum-gauze, to within 2 or 3 mm. of the lower end of the jacket J. Beads may be used, but the balls are much better, and they are more easily cleaned and dried.

It is to be observed that the tube T, containing the liquid in contact with the thermometer bulb, is well protected, being almost entirely surrounded by the vapor which, in turn, is surrounded by a solution of exactly the same concentration, and, consequently, boiling at the same temperature as the solution in the tube. The liquid boiling in the flask is of course super-heated, but the vapor passing up through the notches can hardly super-heat the liquid in the tube T, as the superheating would have to take place at the surface of the bubbles where evaporation can also take place.

On heating the liquid to boiling, the thermometer rises very slowly until the liquid in the flask begins to boil, and bubbles begin to pass through the notches in the stopper C, when it rises very quickly, and is constant in ten or twelve minutes. Not only does the thermometer quickly become constant, but it remains constant, even if the heat applied to the flask is varied much more than it ever need be during a determination. The heat may be increased three or fourfold, until the boiling is changed from gentle to almost violent, but the thermometer remains almost stationary. The apparatus has been put to this test again and again; the greatest elevation being 0.004°.

Few changes have been found necessary or advisable in this apparatus, although it has been in use in this laboratory for two years. The jacket J, was considered unnecessary, at least for all ordinary work and has been discarded. This made the small tube *t*, attached to the stopper C, unnecessary, as the liquid in the flask and tube T, could communicate at once through small holes *h–h* (Fig. 3). The tube T, is extended below the stopper C, to collect bubbles rising from the bottom of the flask.

The apparatus as now manufactured[1] is shown in Fig. 4. The flask rests upon a piece of wire gauze, which rests upon a piece of glass tubing, which serves as a jacket for the Bunsen burner. A very small flame, with the air entirely turned off, is sufficient. The solvent is weighed out in the boiling-flask, which is detached from the condenser at the ground-joint J, (Fig. 3), and enclosed by another stopper ground to fit it. The substance is introduced through the condenser.

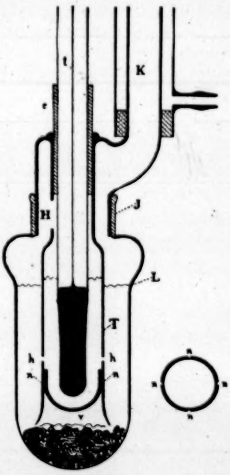


FIGURE 3.

The vital part of the apparatus is the cup-shaped stopper C. This stopper should be carefully ground into place. The ground surface should be 4 or 5 mm. deep. The upper edge of the stopper should be 20 mm. above the lower end of the tube T, in order to secure a steady flow of bubbles through the notches, which should be deep enough for the vapor to pass through them freely, but not so deep that they will exhaust the vapor in the space V, faster than it can be collected. Three notches are sufficient.

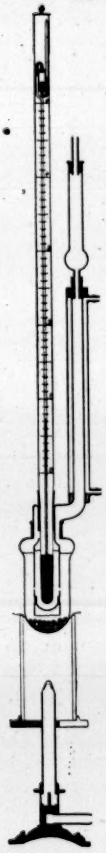


FIGURE 4.

The apparatus will not work with water, as the bubbles cannot force their way through the notches. It does not work with some heavy, high-boiling liquids, probably on account of the great difference in the temperature of the flask and the surrounding air. There are one or two liquids that

[1] By Messrs. Eimer and Amend, New York.

do not work so well if beads are used, but if little balls of platinum gauze are used there is no low-boiling organic liquid so far as the author knows that does not work well.

The following determinations were made by students in this laboratory:

SOLVENT, ALCOHOL: MOLECULAR ELEVATION, 11.5.

Benzoic Acid, 122.

Weight solvent.	Weight substance.	Concentration.	Elevation.	Molecular weight found.	Per cent. variation.
49.110	0.5335	1.09	0.102	122.4	0.3
"	1.0912	2.22	0.195	122.5	0.4
"	1.3397	2.73	0.256	122.5	0.4
48.720	0.6210	1.28	0.120	121.9	0.1
"	0.8510	1.75	0.165	121.8	0.2
49.958	3.0535	6.11	0.573	122.7	0.6
"	3.4630	6.93	0.647	123.0	0.8
"	3.7785	7.56	0.704	123.0	0.8
"	4.0940	8.19	0.764	123.0	0.8
"	4.4850	8.97	0.842	122.6	0.5
"	4.8730	9.95	0.929	123.2	1.0
"	5.3525	10.71	0.994	123.9	1.5
"	5.8415	11.69	1.081	124.4	2.0
"	6.3405	12.68	1.172	124.5	2.0
"	6.7670	13.54	1.247	124.9	2.4

Urea, 60.

Weight solvent.	Weight substance.	Concentration.	Elevation.	Molecular weight found.	Per cent. variation.
34.223	0.3488	1.02	0.185	63.4	5.7
"	0.6724	1.97	0.355	63.6	6.0
"	0.8581	2.51	0.453	63.7	6.2
34.730	0.3233	0.93	0.170	63.0	5.0
34.156	0.3550	1.04	0.188	63.6	6.0
"	0.6945	2.03	0.366	63.9	6.5
"	0.9937	2.91	0.520	64.3	7.2

Acetamide, 59.

Weight solvent.	Weight substance.	Concentration.	Elevation.	Molecular weight found.	Per cent. variation.
31.159	0.2630	0.71	0.165	58.8	0.3
"	0.4500	1.44	0.277	60.0	1.7
31.037	0.2467	0.79	0.153	59.8	1.4
"	0.4711	1.52	0.289	60.4	2.4
"	0.8315	2.70	0.506	60.9	3.2
31.258	0.4171	1.33	0.254	60.4	2.4
"	0.9540	3.05	0.588	60.8	3.1

Acetanilide, 135.

Weight solvent.	Weight substance.	Concentration.	Elevation.	Molecular weight found.	Per cent. variation.
31.854	0.7058	2.21	0.189	134.9	0.1
"	1.0880	3.41	0.289	136.0	0.8
31.580	0.8295	2.62	0.223	135.4	0.3

Benzoic Acid, 122.

Weight solvent.	Weight substance.	Concentration.	Elevation.	Molecular weight found.	Per cent. variation.
47.560	0.4310	0.91	0.085	122.6	0.5
"	0.7152	1.50	0.142	121.8	0.2
"	1.0838	2.28	0.214	122.4	0.2
"	1.3965	2.94	0.276	122.3	0.2
"	1.6232	3.41	0.320	122.6	0.5
"	1.8987	3.99	0.376	122.1	0.1
"	2.1420	4.50	0.422	122.7	0.6
"	2.3848	5.02	0.469	123.0	0.8
"	2.6416	5.55	0.519	123.6	1.3
"	2.9790	6.27	0.579	124.4	2.0

Camphor, 152.

Weight solvent.	Weight substance.	Concentration.	Elevation.	Molecular weight found.	Per cent. variation.
33.667	1.0561	3.14	0.226	160.0	5.0
32.756	1.1371	3.47	0.249	160.0	5.0
55.510	0.1910	0.34	0.026	152.0	0.0
"	0.3272	0.59	0.045	151.0	1.0
"	0.5052	0.91	0.068	154.0	1.0
"	0.9017	1.62	0.120	156.0	3.0
"	1.2644	2.28	0.164	160.0	5.0
"	1.7994	2.34	0.230	162.0	7.0
"	2.2500	4.06	0.286	163.0	7.0
"	2.7142	4.89	0.340	166.0	9.0

SOLVENT, ETHER: MOLECULAR ELEVATION, 21.1.

Camphor, 152.

Weight solvent.	Weight substance.	Concentration.	Elevation.	Molecular weight found.	Per cent. variation.
29.540	0.7480	2.53	0.348	152.7	0.5
"	0.9666	3.28	0.450	153.4	0.9
"	1.2476	4.22	0.580	153.6	1.1
"	1.5268	5.17	0.706	154.3	1.5
"	1.8954	6.42	0.876	154.6	1.7

Iodine, I_2, 253.1.

Weight solvent.	Weight substance.	Concentration.	Elevation.	Molecular weight found.	Per cent. variation.
31.048	2.0970	6.75	0.560	254.5	0.6
31.678	0.9152	2.89	0.241	252.9	0.1
"	1.5252	4.81	0.400	254.0	0.4

Naphthalene, 128.

Weight solvent.	Weight substance.	Concentration.	Elevation.	Molecular weight found.	Per cent. variation.
33.093	0.2830	0.86	0.140	128.9	0.7
"	0.5323	1.61	0.263	129.0	0.8
"	0.7683	2.32	0.379	129.3	1.0
"	0.8884	2.67	0.437	129.6	1.2
"	1.1036	3.35	0.542	129.9	1.5
"	1.3141	3.97	0.643	130.3	1.8
"	1.5288	4.62	0.745	138.8	2.2

SOLVENT, BENZENE: MOLECULAR ELEVATION, 26.7.

$(PNCl_2)x$.[1]

Weight solvent.	Weight substance.	Concentration.	Elevation.	Molecular weight found.	Per cent. variation from 464.
37.618	1.1620	3.09	0.177	466.0	0.4
"	1.4820	3.94	0.227	463.0	0.2
37.987	1.1107	3.92	0.167	467.0	0.7

In conclusion, the author wishes to express his thanks to Professor Remsen, under whose immediate supervision the work above described was carried on.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY, February, 1895.

Contributions from the Chemical Laboratory of Cornell University.

A NEW APPARATUS FOR THE DETERMINATION OF MOLECULAR WEIGHTS BY THE BOILING-POINT METHOD.

W. R. ORNDORFF AND F. K. CAMERON.

Since Beckmann first proposed the apparatus, now so well known by his name, for the estimation of molecular weights from the elevation of the boiling-points of solutions, many modifications have been suggested, and recently, Beckmann[2]

[1] Determined for Dr. H. N. Stokes. See This Journal, 17, 288.

[2] Ztschr. phys. Chem., 15, 656.

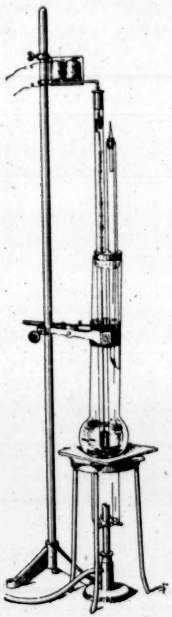
himself has reviewed those descriptions of which have from time to time appeared in the literature.

The advantages of the boiling-point over the freezing-point method are many. In the first place, *any* solvent may be used and the precautions necessary to secure good results are far less numerous.[1] The solubility of substances is much greater at the boiling-point of the solvents than at their freezing-points, and there is no chance for the introduction of errors from some of the dissolved substance crystallizing out, as is the case with the freezing-point method. Notwithstanding these and other advantages of the boiling-point method, it has not been much used owing to the fact that with the apparatus hitherto proposed the time necessary for the determinations has been very great, so that, unless one selects a day when the barometer is practically constant, errors due to barometric changes cannot be avoided. A quick method of determining boiling-points would, of course, eliminate these errors, and would have the additional advantage of saving much time. In the course of an investigation by us it was necessary to make some molecular-weight determinations by the boiling-point method, using solvents of relatively high boiling-points. It soon became evident that the forms of apparatus as yet suggested, were not suited to our purpose, principally, in that stoppers of cork or rubber were acted on to such a degree by the solvents, as to completely interfere with the determinations. Moreover, glass stoppers were precluded because the unequal expansion of the stopper and neck of the vessel, prevented a tight joint, allowing the boiling liquid to distil off in quite appreciable amounts. Stoppers of asbestos and of plaster of Paris (mixed with water-glass) were also tried, and found either to leak or to be acted upon by the solvent.

As a result of our efforts to overcome these and other difficulties, we succeeded in devising an apparatus which worked in such a satisfactory manner with both high and low-boiling liquids and is withal so simple in construction, and readily assembled, that we present here a description with some determinations which will, we believe, demonstrate its useful-

[1] See in this connection: Loomis Physical Review, 1, 199; and Nernst and Abbeg, Ztschr. phys. Chem., 15, 681.

ness to others. There is no part, save perhaps the differential thermometer, but will be found in any well equipped chemical laboratory.



In detail, the apparatus of which a one-eighth scale drawing is given, consists of:

A bulbed flask, made by cutting off the mantle or outer jacket used in the Victor Meyer vapor-density method, to form a vessel about 30 cm. in length and 4 cm. in diameter. Preferably a tube with thin walls and narrow bulb should be selected.

A layer of some heavy material in the bottom of the vessel. This layer should be of some depth, a good conductor of heat, of as dense material as possible, and with roughened surfaces. Broken garnets, pellets of silver, etc., were tried by us, but the best results were obtained with pellets, made by rolling together, strips of scrap platinum, having the surfaces etched with *aqua regia*. Scrap platinum is to be found in every laboratory, is readily cleaned and prepared for a new determination by simple ignition, and works especially well because it is such a good conductor of heat, and has such a high specific gravity. With a bulb of comparatively thin glass and from 30 to 40 grams of platinum pellets, very regular boiling can be obtained, fully as good as with the platinum wire fused into the bottom of the flask, and without the attendant weakening of the vessel.

A condenser, consisting of a straight tube about 13 mm. diameter, the lower end ground with a slant, so as to direct the returning solvent away from the thermometer. When properly adjusted, the lower end of this condenser tube will just touch the outer wall of the flask, returning the cooled solvent in such a way as to have a minimum effect upon the

thermometer readings. The upper end of this condenser was fitted with a stopper carrying a tube[1] with a capillary orifice. When very volatile liquids were used the condenser tube was lengthened, and the upper portion surrounded with a cold-water jacket in the usual manner. But in the case of higher boiling liquids (over 100° C.), it was usually sufficient to have it about the same height as the thermometer, with greatly increased convenience, since the material whose molecular weight was to be determined, was introduced through this tube.

The thermometer was a Beckmann differential instrument of the usual form, made by Göetze, of Leipzig. We found that the instruments furnished for boiling-point determinations are generally constructed with so fine a capillary tube that there is always more or less sticking of the mercury thread, and if the thermometer be struck sufficiently hard to prevent this, there is danger of the thread breaking, necessitating a resetting of the thermometer and a reweighing of the solvent. We therefore used thermometers made for freezing-point determinations, which have larger capillary tubes, precluding any sticking of the mercury, and what is very important, allowing the instrument to set rapidly. The large mercury bulbs of these instruments are undesirable for this work as they require a large amount of solvent and show a very appreciable aneroid barometer effect. These disadvantages are more than compensated for, however, by the increased sensitiveness of the instrument.[2] The thermometer and condenser tube are held in place by a rubber stopper fitted into the flask. In working with volatile liquids, which act upon rubber, an ordinary cork was substituted.

An outer mantle which surrounds the bulb of the flask, and reaches to about a centimeter above the surface of the boiling liquid. The mantle is not figured in the accompanying illustration. Wrappings of asbestos paper, asbestos cloth, and the non-conducting covers used on steam pipes[3] were all tried

[1] When working with hygroscopic solvents this is replaced by a calcium chloride tube.

[2] Directions have been sent to Göetze for a differential thermometer, to be used for boiling-points, in which these difficulties will be obviated.

[3] The non-conducting steam pipe covers made by Keasbey and Mattison, of Philadelphia, of porous magnesia and asbestos, were found to be particularly efficient.

with success. For convenience of manipulation, together with effectiveness, a scarf of asbestos cloth, which can be wrapped very closely around the bulb in four or five folds, is to be preferred.

A small electric hammer, operated by a current from a Daniell cell or gravity battery, was so mounted as to strike continuously the metal top of the thermometer.[1] By removing the gong from a small electric call-bell, a very good hammer for this purpose may be obtained. The thermometer was thus rendered extremely sensitive, making it necessary that the room should be free from draughts, and that the supply of heat should be approximately constant.

A source of heat, for which purpose was utilized a Bunsen burner of appropriate size, fitted with a glass chimney to protect the flame as much as possible from irregular draughts. As a rule an Elsler gas regulator for constant pressure, and a precision stop-cock were used. Experiments to determine their value indicated that they were not necessary. The size of the flame, which should be rather large than small, can be well regulated by using a Hofmann pinch-cock on the rubber tube connecting the burner with the gas supply. For very volatile liquids a small flame was obtained by drawing out a glass tube to proper size, and passing it through a cork fitted to the tube of the Bunsen burner.

The whole apparatus was clamped into position in the following way: A strip of fine copper gauze, about 4 cm. in width, was wrapped to several thicknesses, smoothly and tightly about the tube, and this was then firmly clamped (using naked metallic surfaces) to an iron stand. There was thus obtained a condenser, of large heat capacity and good radiating surface, to take the heat from the walls of the tube. This device was found to be quite efficient, and, in the case of the higher-boiling liquids, but very little of the solvent condensed above this guard. The bottom of the bulb rested upon a piece of fine copper gauze, slightly moulded to receive it, and this in turn was fitted over a circular orifice, of from 3 to 4 cm. in diameter, cut into heavy asbestos board.

The boiling of the liquid should be *quite rapid*, and to this

[1] Loomis (Physical Review, 1, 206) made use of a similar device in his freezing-point determinations, and calls attention to the necessity for its use.

end, as large a flame should be used as the conditions of the experiment will permit. We have found this to be a very important point for the successful use of this apparatus, and, after much time spent in experimenting, have shown that the best results are obtained when the liquid is boiled as rapidly as possible, without driving the solvent too far up the condenser tube. The excess of heat is thus removed by the condenser, and slight variations in the heat supply, due to increased or diminished gas pressure, or to air currents, have very little influence on the readings of the thermometer. The boiling of the solvent should be continued for about an hour, in order that the materials, of which the thermometer is constructed, may adjust themselves so that constant readings may be obtained. But this condition once reached, the determination may be made quickly and with precision, as the thermometer under the electric hammer is extremely sensitive and sets very rapidly. Usually, from two to three minutes after introducing some of the substance, very good readings could be obtained. Apparently, in some cases, the thermometer steadied and became constant more readily after the introduction of a small quantity of the material under examination, and this device was occasionally used.

The material of which the molecular weight is to be determined was introduced in the form of compressed tablets, made in the manner suggested by Beckmann. It is very desirable, whenever possible, that a liquid in which the material is readily soluble should be used. Much of the accuracy of the method depends upon the rapidity with which the thermometer sets, and the readings are taken, because errors due to changes in the barometric pressure are thus avoided. However, when from the nature of the case solvents of slight power must be used, we found it desirable to grind the solid material in an agate mortar, with alcohol (or some other readily volatile medium), to a thick paste, which was then moulded in the usual way and dried to constant weight in an air-bath. The tablets thus prepared are extremely fragile but can be handled with care, and usually crumble to a very fine powder on coming in contact with the boiling solvent, thus presenting a very large surface to its action.

That it is distinctly advantageous to make such determinations when the barometer is constant, or as nearly so as possible, goes without saying.

The readings were taken with a telescope provided with cross hairs and leveling adjustment, located about two meters from the thermometer scale. For ordinary work, however, readings made with a simple magnifying glass would be sufficiently accurate. The room was kept as free as possible from draughts, and to further eliminate this disturbing influence, the lower part of the apparatus was at times partially surrounded with a wooden box with good effect.

All the materials used in the determinations here recorded were very carefully purified before being used. The boiling-points of the solvents given are determinations made with a standardized thermometer which was entirely surrounded with the vapor of the boiling liquid.

When the latent heat of vaporization was known, it was used in calculating the molecular rise of the solvent, according to the well-known formula[1] of Van't Hoff-Arrhenius, In other cases we used the experimentally determined constant. The observations for the whole series of determinations were *always* taken before any of the results were calculated, so as to prevent, as far as possible, any prejudiced readings. The time required to make a series of determinations, after the thermometer had become constant, is given for each substance, though it is to be understood that this does not represent the shortest time in which it was possible to complete the series, for in many cases we purposely waited much longer than necessary to see if the readings of the thermometer would change. The average length of time for a series of six or eight determinations was about thirty minutes.

In the following tables we give the results obtained with this apparatus with low and high boiling liquids. The work in which carbon bisulphide, benzene, toluene, and naphthalene were used was done by Mr. G. L. Terrasse, an undergraduate student of this university, to whom we wish here to express our thanks.

The molecular weight and the molecular elevation of infi-

[1] Molecular rise $= \frac{0.0198\ T^2}{H}$, T being the absolute boiling-point at 760 mm., and H the latent heat of vaporization.

nite dilution are given in each case, as well as the averages of the whole series of determinations. When the individual determinations do not differ very much from each other the averages are to be preferred, otherwise the molecular weight at infinite dilution is more reliable.

It is especially to be noted in connection with the following tables that the results are recorded exactly as they were observed. *No single determination has been omitted, nor has any series been eliminated.*

SOLVENT: CARBON DISULPHIDE.

Boiling-point, 46°.0 C. at 757.4 mm.
Molecular elevation for 100 grams, 23°.75.
Latent heat of vaporization 84.82 Cal. Regnault, 1862.

Naphthalene, 128.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
128.47	0.5603	0°.082	24°.1	126
"	1.0495	0 .154	24 .1	127
"	1.5187	0 .222	24 .0	127
"	2.0388	0 .297	24 .0	127
"	2.5553	0 .370	23 .8	128
"	3.0343	0 .439	23 .8	128
"	3.5522	0 .517	24 .0	127
"	4.1600	0 .605	23 .9	127
	At infinite dilution,		*24 .0*	*127*
	Average of determinations,		*24 .0*	*127*

Time, 40 minutes. Barometer, 749.2–749.3 mm.

SOLVENT: CHLOROFORM.

Boiling-point, 60°.2 at 741.7 mm.
Molecular elevation for 11 grams, 36°.6.
Latent heat of vaporization, 61.0 Cal. Regnault, 1862.

Naphthalene, 128.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
204.00	0.6964	0°.100	37°.4	125
"	1.3532	0 .190	36 .6	128
"	2.0996	0 .298	37 .0	127
"	2.8397	0 .384	35 .3	133
"	3.4233	0 .452	34 .3	135
"	4.4750	0 .590	34 .4	136
	At infinite dilution,		*37 .5*	*121*
	Average of determinations,		*35 .9*	*131*

Time, 30 minutes. Barometer, 758.6–758.3 mm.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
204.01	0.7142	0°.096	35°.1	133
"	1.3671	0 .186	35 .6	132
"	2.0055	0 .275	35 .9	131
"	2.5902	0 .362	36 .5	128
"	3.4636	0 .480	36 .3	129
"	4.7272	0 .656	36 .3	129
	At infinite dilution,		*34 .7*	*134*
	Average of determination,		*36 .0*	*130*

Time, 30 minutes. Barometer, 756.7–756.6 mm.

SOLVENT: BENZENE.

Boiling-point, 79°.6 C. at 744.5 mm.
Molecular elevation for 100 grams, 26°.6.
Latent heat of vaporization, 93°.4 Cal. Schiff, 1886.

Naphthalene, 128.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
91.986	0.2657	0°.053	23°.5	145
"	0.6388	0 .128	23 .6	144
"	1.0180	0 .205	23 .7	144
"	1.3995	0 .282	23 .7	144
"	1.8481	0 .378	24 .1	141
"	2.3384	0 .480	24 .2	141
"	2.9719	0 .612	24 .2	141
"	3.6349	0 .742	24 .0	142
	At infinite dilution,		*23 .6*	*144*
	Average of determinations,		*23 .9*	*143*

Time, 60 minutes. Barometer, 736.3–735.7 mm.

SOLVENT: TOLUENE.

Boiling-point, 109°.7 at 741.7 mm.
Molecular elevation for 100 grams, 35°.1.
Heat of vaporization, 83.55 Cal. Schiff.

Naphthalene, 128.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
83.88	0.7318	0°.210	30°.8	145
"	1.4428	0 .405	30 .1	149
"	2.1202	0 .602	30 .5	147
"	3.1532	0 .897	30 .5	147
"	4.0997	1 .166	30 .5	147
"	5.0883	1 .448	30 .6	147
"	6.2043	1 .756	30 .4	148
"	7.3067	2 .061	30 .3	148
	At infinite dilution,		*30 .5*	*147*
	Average of determinations,		*30 .5*	*147*

Time, 45 minutes. Barometer, 736.4–736.2 mm.

SOLVENT: PYRIDINE.

Boiling-point, 114°.2 C. at 741.7 mm.
Molecular weight for 100 grams, 26°.9.

Anthracene, 178.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
89.90	0.1467	0°.026	28°.2	170
"	0.2749	0 .049	28 .5	168
"	0.6554	0 .110	26 .9	178
	At infinite dilution,		*27 .9*	*173*
	Average of determinations,		*27 .8*	*172*

Time, 30 minutes. Barometer, 749.9 mm. constant.

Triphenylmethane, 244.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
87.22	0.6458	0°.074	24°.4	270
"	0.9432	0 .118	26 .6	247
"	1.1507	0 .145	26 .8	246
	At infinite dilution,		*25 .8*	*252*
	Average of determinations,		*25 .9*	*254*

Time, 30 minutes. Barometer constant.

SOLVENT: ETHYLENE BROMIDE.

Boiling-point, 128°.8 C. at 741.7 mm.
Molecular elevation[1] for 100 gram, 63.2°.

Anthracene, 178.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation fonnd.	Molecular weight found.
217.28	0.2142	0°.034	61°.4	182
"	0.3919	0 .063	62 .2	181
"	0.6704	0 .110	63 .5	177
"	1.1170	0 .184	63 .7	176
	At infinite dilution,		*63 .2*	*178*
	Average of determinations,		*62 .7*	*179*

Time, 25 minutes. Barometer, 749–748.5 mm.

Triphenylmethane, 244.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
204.07	0.2659	0°.031	58°.1	265
"	0.5629	0 .073	64 .6	239
"	0.8599	0 .106	61 .4	251
"	1.1957	0 .161	67 .0	230
"	1.5888	0 .215	67 .3	229
	At infinite dilution,		*62 .7*	*246*
	Average of determinations,		*63 .7*	*243*

Time, 40 minutes. Barometer, 744.0–743.9 mm.

[1] This is the same constant that Beckmann obtained. Ztschr. phys. chem., 6, 462.

SOLVENT: ANISOL.

Boiling-point, 152°.7 at 741.7 mm.
Molecular elevation for 100 grams, 44°.3.

Acetanilid, 135.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
100.23	0.7783	0°.258	44°.8	133
"	1.4713	0 .460	42 .3	141
"	2.0654	0 .631	41 .3	145
	At infinite dilution,		*45 .8*	*130*
	Average of determinations,		*42 .8*	*139*

Time, 60 minutes. Barometer, 748.3–748.7 mm.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
100.23	0.7482	0°.224	40°.5	147
"	1.2959	0 .370	38 .6	154
"	1.7435	0 .490	38 .0	157
"	2.2073	0 .610	37 .4	159
"	2.6673	0 .720	36 .5	163
"	3.0613	0 .814	36 .0	166
	At infinite dilution,		*43 .7*	*137*
	Average of determinations,		*37 .8*	*157*

Time, 60 minutes. Barometer, 747.2–747.3 mm.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
99.84	0.5514	0°.165	40°.3	148
"	1.0747	0 .310	38 .9	153
"	1.5692	0 .455	39 .1	152
"	2.0467	0 .565	37 .2	160
"	2.4447	0 .670	37 .2	161
"	2.8532	0 .760	35 .9	166
	At infinite dilution,		*41 .8*	*143*
	Average of determinations,		*38 .1*	*157*

Time, 60 minutes. Barometer, 739.7 mm. constant.

Anthracene, 178.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
104.96	0.5044	0°.110	41°.1	194
"	1.0140	0 .215	40 .0	199
"	1.4972	0 .320	40 .3	197
"	1.9666	0 .415	39 .8	200
"	2.4394	0 .515	39 .8	200
"	2.9144	0 .703	45 .5	175
	At infinite dilution,		*44 .0*	*180*
	Average of determinations,		*41 .1*	*194*

Time, 60 minutes. Barometer 738.3–737.3 mm.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
94.73	0.6162	0°.172	47°.1	168
"	1.1898	0 .290	41 .9	188
"	1.7194	0 .402	39 .4	200
	At infinite dilution,		*43 .4*	*182*
	Average of determinations,		*42 .8*	*185*

Time, 25 minutes. Barometer, 737.2–737.3 mm.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
101.95	0.3800	0°.094	44°.9	176
"	0.7927	0 .194	44 .4	178
"	1.2089	0 .285	44 .8	184
	At infinite dilution,		*45 .0*	*175*
	Average of determinations,		*44 .0*	*179*

Time, 30 minutes. Barometer constant.

Triphenylmethane, 244.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
100.27	1.0883	0°.200	44°.9	240
"	1.5397	0 .280	44 .5	243
"	2.0093	0 .370	45 .1	240
"	2.3917	0 .430	44 .0	246
"	2.7931	0 .510	44 .7	242
	At infinite dilution,		*44 .3*	*244*
	Average of determinations,		*44 .6*	*242*

Time, 55 minutes. Barometer, 745.4–745.8 mm.

SOLVENT: PHENETOL.

Boiling-point, 167°.9 C. at 741.9 mm.
Molecular elevation for 100 grams, 49°.3.

Anthracene, 178.

Grams Solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
90.33	0.4788	0°.145	48°.7	180
"	0.7615	0 .232	48 .9	179
"	0.9930	0 .310	50 .2	175
"	1.2714	0 .395	50 .0	175
	At infinite dilution,		*48 .5*	*182*
	Average of determinations,		*49 .5*	*177*

Time, 50 minutes. Barometer, 739.3–739.6 mm.

Triphenylmethane, 244.

Grams solvent.	Grams substance.	Observed elevation.	Molecular elevation found.	Molecular weight found.
82.92	0.3182	0°.081	51°.5	233
"	0.5751	0 .139	48 .9	245
"	0.8812	0 .208	47 .8	251
"	1.1889	0 .288	49 .0	245
"	1.4239	0 .343	48 .8	246
"	1.7367	0 .415	48 .3	248
"	1.9996	0 .474	48 .0	250
"	2.2680	0 .540	48 .2	249
	At infinite dilution,		*49 .2*	*244*
	Average of determinations,		*49 .2*	*246*

Time, 45 minutes. Barometer, 743.2 mm. constant.

SOLVENT: NAPHTHALENE.

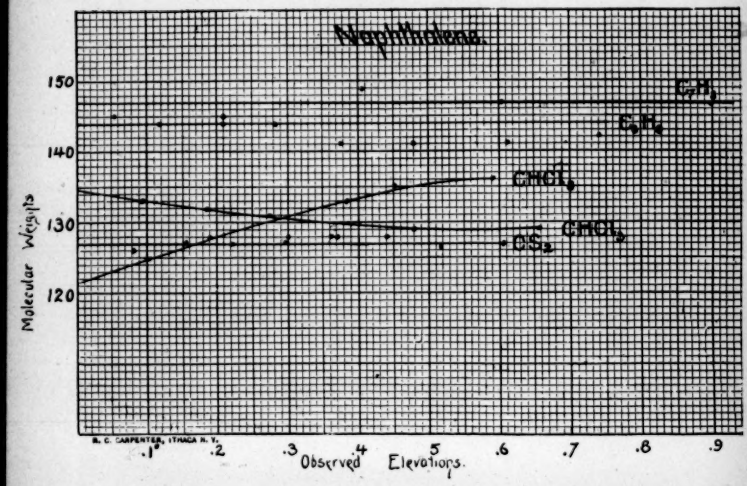
Boiling-point, 216°.7 C. at 741.9 mm.
Molecular elevation for 100 grams, 60°.7.

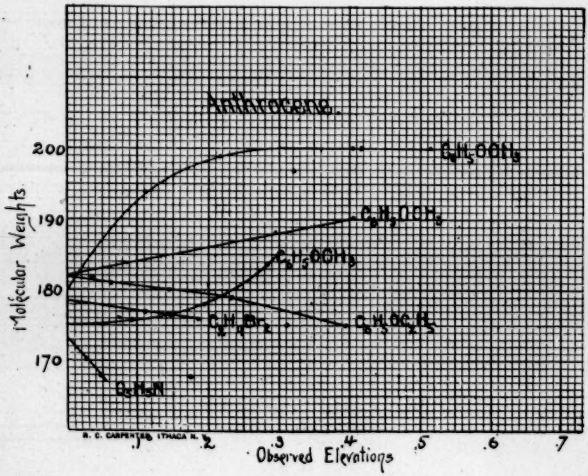
Triphenylmethane, 244.

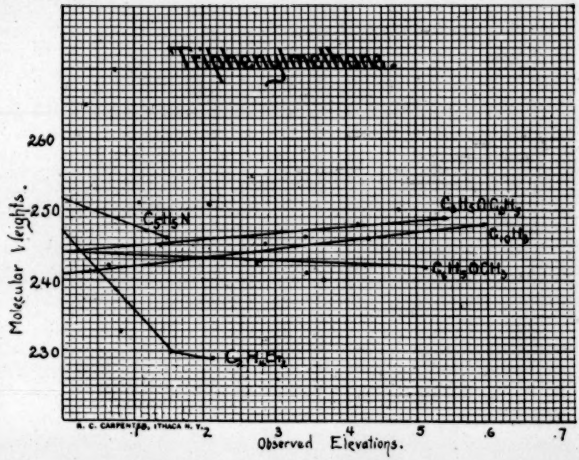
Grams solvent.	Grams substance.	Observed elevation	Molecular elevation found.	Molecular weight found.
89.75	0.2330	0°.065	61°.1	242
"	1.2315	0 .346	61 .5	241
"	1.5290	0 .428	61 .3	242
"	1.8554	0 .508	60 .0	247
"	2.1803	0 .593	59 .6	248
	At infinite dilution,		*61 .5*	*241*
	Average of determinations,		*60 .7*	*244*

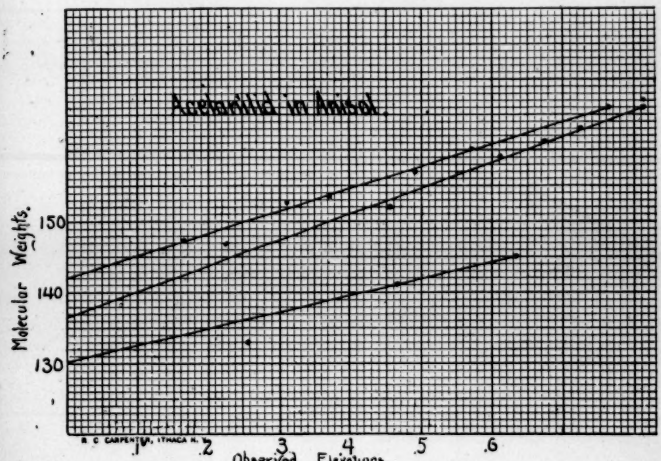
Time, 40 minutes. Barometer, 735.7 mm. constant.

For the sake of completeness and to compare these results with those of others, they are here presented in a graphic form. The observed elevations are taken as abscissas and the molecular weights as ordinates. Each chart being for a single substance, with the solvents indicated by their formulas. The scales are so selected as to exaggerate the variations in the molecular weights.


Naphthalene.
Molecular Weights
150
140
130
120
C_7H_8
C_6H_6
$CHCl_3$
CS_2
$CHCl_3$
R. C. CARPENTER, ITHACA N. Y.
.1
.2
.3
.4
.5
.6
.7
.8
.9
Observed Elevations.


Anthracene.
Molecular Weights
200
190
180
170
$C_6H_5OCH_3$
$C_6H_4(OCH_3)_2$
$C_6H_3(OCH_3)_3$
$C_6H_2(OCH_3)_4$
C_6H_5OH
R. C. CARPENTER, ITHACA N. Y.
.1
.2
.3
.4
.5
.6
.7
Observed Elevations


Triphenylmethane.
Molecular Weights.
260
250
240
230
C_5H_5N
$C_6H_5OC_6H_5$
C_6H_6
$C_6H_5OCH_3$
C_6H_5Cl
R. C. CARPENTER, ITHACA N. Y.
.2
.3
.4
.5
.6
.7
Observed Elevations.


Acetanilid in Anisol.
Molecular Weights.
150
140
130
R. C CARPENTER, ITHACA N. Y.
.2
.3
.4
.5
.6
Observed Elevations.

GLUTARIMIDE.

By R. Seldner.

The reaction of Gautier[1] by which diacetamide is formed on heating acetonitrile and acetic acid together, has been applied to a number of other nitriles and monatomic acids, both of the fatty and of the aromatic series, by Colby and Dodge.[2] The results obtained showed the formation in most cases of mixed secondary amides. Miller[3] has published the results of some experiments with succinic acid and its nitrile. He tried three different combinations; first, succinic acid and acetonitrile; second, succinic nitrile (ethylene cyanide) and acetic acid; and third, succinic acid with succinic nitrile. These three sets of experiments all gave the same product, succinimide.

It seemed to the writer desirable to try parallel reactions with glutaric acid, the next member of the series, and its nitrile. The glutaric nitrile was made by the method used by Fauconnier[4] for preparing ethylene cyanide. A concentrated aqueous solution of potassium cyanide was slowly added to a boiling alcohol solution of trimethylene bromide. After boiling for some time, the alcohol and water were distilled off and the nitrile extracted from the dry residue with absolute alcohol. The alcohol was now evaporated under diminished pressure and the nitrile remaining was twice distilled *in vacuo*. It all distilled over between 150° and 180° at a pressure of 40 mm. and condensed to a clear, colorless liquid having a faint odor. To prepare glutaric acid, a portion of the nitrile was heated for some time with concentrated hydrochloric acid, and the solution finally evaporated to dryness. The impure glutaric acid was extracted from the dry residue with ether, decolorized with bone-black, and recrystallized from ether. It then formed clear, colorless prisms, melting at 98°. The acetonitrile used was purchased of Kahlbaum, Berlin, and was rectified over phosphorus pentoxide before use.

Three different combinations were made:

[1] Ztschr. Chem., 1869, 127.
[2] This Journal, **13**, 1, (1891).
[3] J. Am. Chem. Soc., **16**, 443 (1894).
[4] Bull. Soc. Chim. (Paris), **30**, 214.

First Experiment.—6.6 grams of glutaric acid (1 molecule) and 4.1 grams of acetonitrile (2 molecules).

Second Experiment.—4.7 grams of glutaric nitrile (1 molecule) and 6.0 grams acetic acid (2 molecules).

Third Experiment.—6.6 grams glutaric acid and 4.7 grams glutaric nitrile (equal molecules).

The mixtures were introduced into strong glass tubes and 2 to 5 drops acetic anhydride added to each. The glass tubes were then sealed, placed in an oven, and heated. After heating for three hours at 180°, the contents of the tubes showed but little change. Four hours' further heating at 200° gave evidence of a reaction in the second and third tubes; they were therefore taken out and the first tube was heated five hours longer at 210.° All three tubes were now opened; slight pressure was noticed on opening. The contents were removed and washed with ether. The residues were then dissolved in alcohol, the solutions decolorized with bone-black, and concentrated to crystallization. The crystals obtained were recrystallized from alcohol and were then perfectly colorless and evidently pure. The amounts obtained from the three tubes were, respectively: first, 4.0 grams; second, 2.25 grams; and third, 5.4 grams. The crystals from the three tubes were identical in appearance. They formed thin square or rectangular plates with a fine lamellar cleavage.

The melting-points of the three sets of crystals were found to be:

I, at 153°; II, at 152.8°; III, at 152.5°.

The melting-point of glutarimide as given by Bernheimer[1] is 151° to 152°. Wolffenstein,[2] who obtained it by oxidizing piperidine with hydrogen peroxide, gives the melting-point as 154.5°.

The following elementary analyses were made:

Crystals I. 0.0780 gram substance gave 0.0430 gram H_2O and 0.1525 gram CO_2.

Crystals II. 0.0774 gram substance gave 0.0432 gram H_2O and 0.1510 gram CO_2.

Crystals III. 0.0989 gram substance gave 0.0548 gram H_2O and 0.1922 gram CO_2.

[1] Gazz. chim. ital., **12**, 281. [2] Ber. d. chem. Ges., **25**, 2777.

0.0995 gram substance gave 11.3 cc. N at 25° and 755.3 mm.

	I.	II.	III.	Theory for $(CH_3)_2.(CO)_2.NH$.
C	53.32	53.20	53.00	53.10
H	6.13	6.20	6.16	6.19
N	....	....	12.57	12.39

The crystals were insoluble in ether and in benzene. An attempt was made to determine their molecular weight by Raoult's method, glacial acetic acid being used as solvent. The results obtained were very irregular.

10.6646 grams $HC_2H_3O_2$ used as solvent. With 0.0558 gram product dissolved, the freezing-point was lowered 0.1745°, corresponding to the molecular weight of 116.9.

With 0.1066 gram product dissolved the freezing-point was lowered 0.3425°, corresponding to the molecular weight of 113.8.

With 0.1564 gram product dissolved no constant freezing-point could be obtained, as the depression increased at each reading.

With 0.2060 and 0.2603 gram product in solution the freezing-point was also erratic.

The theoretical molecular weight for glutarimide is 113.

The products were further proved to be glutarimide by heating weighed quantities with concentrated hydrochloric acid, and determining the amounts of ammonia and glutaric acid formed. The ammonia was estimated by precipitation with platinic chloride.

0.2001 gram substance gave 0.1681 gram Pt = 0.0293 gram NH_3; theory would require 0.0301 gram NH_3.

The glutaric acid was determined by evaporating to dryness, and exhausting the thoroughly dried residue with absolute ether. The ether was evaporated and the residue weighed after drying at 100°.

0.1974 gram substance gave 0.2274 gram glutaric acid; theory requires 0.2306 gram.

Glutarimide is therefore the principal product in all three experiments.

In experiment I, if the materials reacted parallel with those of Gautier:

$$CH_3COOH + CH_3CN = \underset{\text{Diacetamide}}{\begin{matrix} CH_3—CO \\ CH_3—CO \end{matrix}\!\!>NH};$$

there would result:

$$CH_2\begin{matrix}/CH_2.COOH\\ \backslash CH_2.COOH\end{matrix} + 2CH_3CN = CH_2\begin{matrix}/CH_2.CO.NH.CO.CH_3\\ \backslash CH_2.CO.NH.CO.CH_3\end{matrix}$$

Sym. Diacetylglutaramide

and in experiment II:

$$CH_2\begin{matrix}/CH_2.CN\\ \backslash CH_2.CN\end{matrix} + 2CH_3COOH = CH_2\begin{matrix}/CH_2.CO.NH.CO.CH_3\\ \backslash CH_2.CO.NH.CO.CH_3\end{matrix}$$

Sym. Diacetylglutaramide

Since glutarimide was produced in large quantity in each tube, the reactions probably took place thus:

I. $$CH_2\begin{matrix}/CH_2.COOH\\ \backslash CH_2.COOH\end{matrix} + 2CH_3CN = CH_2\begin{matrix}CH_2.CO\\ CH_2.CO\end{matrix}\!\!>NH +$$

Glutarimide.

$$CH_3COOH + CH_3CN.$$

II. $$CH_2\begin{matrix}/CH_2.CN\\ \backslash CH_2.CN\end{matrix} + 2CH_3COOH = CH_2\begin{matrix}CH_2.CO\\ CH_2.CO\end{matrix}\!\!>NH +$$

Glutarimide.

$$CH_3CN + CH_3COOH.$$

Acetic acid and acetonitrile are left over in both cases. These may have further reacted to form the diacetamide, $(CH_3CO)_2NH$, of Gautier. To determine this point it is proposed to repeat these two experiments.

The best yield of glutarimide was obtained in the third experiment. The materials here have undoubtedly reacted thus:

$$CH_2\begin{matrix}/CH_2.CO.OH\\ \backslash CH_2.CO.OH\end{matrix} + CH_2\begin{matrix}/CH_2.CN\\ \backslash CH_2.CN\end{matrix} = 2CH_2\begin{matrix}/CH_2.CO\\ \backslash CH_2.CO\end{matrix}\!\!>NH.$$

Glutarimide.

It will be interesting to learn if other acids of the malonic series give imides on being heated with nitriles.

LABORATORY OF THE ADELPHI ACADEMY,
BROOKLYN, N. Y., March, 1895.

ON THE OXIDATION OF COMPLEX CARBOHYDRATES.

BY G. DE CHALMOT.

I recently advanced the hypothesis that in plants pentose molecules are formed in complex molecules of hexosans in which a part or all of the aldehyde groups have been bound by condensation, and are thereby preserved from further oxidation. It is probable that pentoses are formed from hexoses by the alcohol group at the end of the hexose molecule being

oxidized to aldehyde and carboxyl, and by the splitting off of carbon dioxide. I have since attempted to make in the laboratory pentosans from hexosans by making use of reactions similar to those which I suppose to take place in the walls of the plant-cells. These reactions are:

1. Oxidation to aldehyde of alcohol groups at the end of hexose groups which are united to complex carbohydrates.
2. Oxidation of these aldehyde groups to carboxyl.
3. Elimination of carbon dioxide from the carboxyl without affecting other parts of the hexose group.

The results which I have obtained concern only the first of these reactions. They are few and incomplete, for the work has been interrupted at an early stage. I shall, however, not return to the subject, and so communicate the results as they are.

Cross, Bevan, and Beadle[1] found that, if different complex carbohydrates, cane-sugar, milk-sugar, starch, cotton-cellulose, are oxidized with chromic acid, they are converted into compounds that yield furfurol, if they are heated with acids. I should not be surprised if these oxidized compounds contain glucuronic acid or its isomer. These compounds have, however, not been obtained in pure condition. I, therefore, sought for an oxidizing agent which would act gently and admit of obtaining oxidation-products of definite chemical composition. For this purpose I used bromine and soda, which have been used by E. Fischer for the oxidation of polyacid alcohols. Fischer thus made *i*-galactose from dulcite, and glycerose from glycerol.

The action of bromine and soda on starch, cane-sugar, cellulose, and α-methyl-*d*-glucoside was tested:

Starch.—5 grams of pulverized starch were mixed with a solution of 11 grams of soda in 60 cc. of water; 5 grams bromine were added and the mixture was shaken until the bromine was dissolved. In a short time carbon dioxide commenced to be given off. After an hour or more the liquid became entirely colorless. The mixture now reduced Fehling's solution in the cold; the starch had been partly liquified.

[1] Ber. d. chem. Ges., **26**, 2523.

The mixture was neutralized with acetic acid, phenylhydrazine hydrochloride added, and the liquid heated on the water-bath. A slight precipitate of an osazone (?) was formed. The aldehyde reactions, which the starch showed after the treatment with bromine and soda, are due to an oxidation and to not hydrolysis, for bromine alone does not perceptibly act on starch in a week. After that time the mixture does not reduce Fehling's solution, not even if the starch has been liquified by boiling with water previous to being treated with bromine. Nor does soda alone act on starch.

Saccharose is also oxidized by bromine and soda, the solution becoming rapidly brown. However, if the solution is not too concentrated, the liquid can be obtained entirely colorless after the reaction is over. This liquid reduces Fehling's solution. Heated under proper conditions with phenylhydrazine, a small amount of osazone was precipitated in the liquid. This was glucosazone (melting-point: 202°; percentage of nitrogen: 15.6).

5.5 grams of α-methyl-*d*-glucoside and 11 grams of soda were dissolved in 60 cc. of water; 5 grams of bromine were added to this solution, and dissolved by shaking. Reaction soon commenced: carbon dioxide was evolved and the liquid became colorless. This liquid reduced Fehling's solution slowly at the temperature of the room, at once at 50°; the solution was neutralized with acetic acid, 5 grams of phenylhydrazine hydrochloride were added, and the liquid then heated on the water-bath. An osazone was precipitated. After cooling, this precipitate was collected. It weighed 0.7 gram. It was brown in color and contained, besides an osazone, at least one hydrazone or hydrazide. By repeated washings with small amounts of absolute alcohol, most of the impurities were removed and the osazone gradually became bright yellow. The osazone is nearly insoluble in cold alcohol. The hydrazone or hydrazide is red-brown, at least when precipitated in an impure condition by water from the alcoholic solution.

The osazone was recrystallized from boiling absolute alcohol. By longer boiling with alcohol, it seemed to be slightly decomposed. It was dried over sulphuric acid. The purest

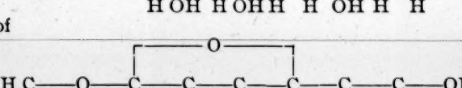
osazone which I obtained was bright yellow with a slight greenish tint. The melting-point was determined beside that of pure *d*-glucosazone. While glucosazone melts at 205°, the new osazone melts at 192°–194°. The osazone contains:

	Calculated for $C_{18}H_{22}N_4O_4$.	Calculated for $C_{18}H_{22}N_4O_4$.	Found.
C	61.62	60.34	61.71
H	5.95	6.15	6.51
N	15.1	15.6	14.6

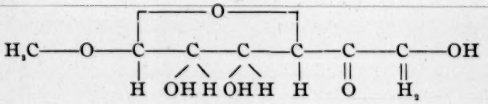
The figures agree fairly with those for *α*-methyl-*d*-glucoside osazone. There is, however, only a slight difference between the percentages of carbon, hydrogen and nitrogen in *d*-glucosazone and in methylglucoside osazone.

Crystals of *d*-glucosazone and of the new osazone were obtained by allowing concentrated alcoholic solutions of both compounds to cool slowly side by side. The crystals are distinctly different, those of *d*-glucosazone being about three times as long. Notwithstanding these results, I do not consider that I have conclusive proofs that the new osazone is *α*-methyl-*d*-glucoside osazone. In order to prove this, the osazone should be decomposed into its component. I was preparing larger amounts of this substance when the work was interrupted.

If the osazone has the formula which I expect it to have, it should be the osazone of a glucoside-ose[1] either of



or of



Cotton-cellulose was extracted with ether, boiled with dilute

[1] The fact that, by the oxidation of a hexite, mostly a ketose and an aldose are formed (E. Fischer: Ber d. chem. Ges., **27**, 3190) should not lead directly to the conclusion that also here a mixture must be formed. The lactone connection, which probably exists between carbon atoms 1 and 4, will probably have an influence on the reaction.

acid, with dilute alkali, and with water, and dried. 5 grams were treated with 11 grams of soda and 5 grams of bromine. The reaction was slow, but, after some hours, the color of the bromine disappeared entirely. The cotton fibres retained their outer form. They were washed with water. They did not reduce Fehling's solution at the temperature of the room, but they reduced it at 100°. The cuprous oxide was precipitated on and in the fibres, which could be very nicely observed under the microscope. This cellulose thus showed one of the properties of the oxycelluloses of Cross, Bevan, and Beadle.[1] Further tests were not made.

SPRAY, NORTH CAROLINA.

ON THE DETERMINATION OF FORMIC ACID BY TITRATION WITH POTASSIUM PERMANGANATE.

BY HARRY C. JONES.

Péan de Saint-Gilles[2] determined formic acid by titration with a standard solution of potassium permanganate in the presence of an alkaline carbonate. Lieben[3] has shown that this titration can be carried to the end, satisfactorily, in the presence of the alkaline carbonate, the end being indicated by the appearance of color, due to the presence of a small quantity of unreduced permanganate. The principle is the same as that of Saint-Gilles, but the experimental work is more elaborate. Lieben states that the method has a slight drawback when the solution containing the formic acid is cold. The precipitate formed from the reduction of the permanganate does not settle quickly, and this renders it difficult to determine at once, whether the supernatant liquid is clear, or contains a trace of permanganate. It was found that by warming the solution on a water-bath, time was saved in determining the end of the reaction, without sacrificing the accuracy of the method. The method, as carried out by Lieben, seems to have yielded satisfactory results, yet it is well known that the color produced by a small amount of permanganate will gradually disappear if the solution stands in contact with the precip-

[1] Ber. d. chem. Ges., **27**, 1061.

[2] Ann. chim. phys. [3], **55**, 374, (1859). [3] Monatsh. Chim., **14**, 746, (1893).

itated manganese hydroxide. This would render it difficult to determine always, the true end of the above reaction, especially when there is a large amount of formic acid present, giving rise to much of the manganese precipitate.

The method, which I employed in this laboratory for determining formic acid, does not differ in principle from the one above considered, but the procedure in making the titrations seems to be preferable to that employed by Lieben. The work in question was carried out in 1891, the same year in which Lieben states that he began his work along this line, in connection with an investigation suggested to the author by Prof. Remsen. The method is as follows: the solution containing the formic acid was made alkaline with sodium carbonate, warmed, and treated with an *excess* of a standard solution of potassium permanganate. All the formic acid was oxidized to carbon dioxide and water, and a heavy precipitate of manganese hydroxide was thrown down. The alkaline solution was then acidified with sulphuric acid, and a measured volume of oxalic acid run in until all the precipitate had dissolved, and all of the permanganate had disappeared. The excess of oxalic acid was finally titrated with a standard permanganate solution. A volume of oxalic acid, equal to that used, was then measured off, and titrated against the permanganate solution. The difference between the total permanganate used, and that amount which was equivalent to the oxalic acid, was the permanganate required to oxidize the formic acid. Knowing this, the amount of formic acid present was readily calculated.

To test the accuracy of this method a solution of pure formic acid was prepared, and the acid, in measured volumes, determined by the method just described. The results of these determinations showed that the solution contained the following percentages of formic acid:

Determination	I.	Formic acid,	24.7 per cent.
"	II.	" "	24.9 "
"	III.	" "	25.1 "

The same solution of formic acid was then determined alkalimetrically, against a standard solution of potassium hydroxide, with the following results:

Determination I. Formic acid, 25.1 per cent.
" II. " " 25.3 "

From the specific gravity, the formic acid present was 24.8 per cent.

Péan de Saint-Gilles[1] stated, further, that oxalic and formic acids can be determined in the presence of each other by means of potassium permanganate. The oxalic acid is oxidized by the permanganate in acid solution, while the formic acid is not acted upon under these conditions. The solution is then made alkaline with an alkaline carbonate; sodium carbonate and the formic acid determined by titration with more of the permanganate solution. This seemed to me to be rather doubtful from my own experience with these acids, and was subjected to experimental test. A weighed amount of oxalic acid was mixed with a large amount of formic acid and then an attempt was made to determine the oxalic acid by titration against a permanganate solution. The solution containing the mixture of the two organic acids was acidified with dilute sulphuric acid, and warmed just enough to facilitate the action of the permanganate on the oxalic acid.

0.3870 gram of oxalic acid was mixed with 2.4383 grams of formic acid in a dilute water solution. The oxalic acid found = 0.4235 gram.

0.7287 gram oxalic acid was brought into solution with a large excess of formic acid. The oxalic acid found = 0.9834 gram.

These results show that under these conditions some of the formic acid is also oxidized, and that oxalic acid cannot be determined by the method described by Saint-Gilles, if formic acid be present.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY.

REVIEWS.

THEORETICAL CHEMISTRY. By PROF. WALTER NERNST, PH. D., of the University of Göttingen. TRANSLATED BY PROF. CHARLES SKEELE PALMER, PH. D., of the University of Colorado. With twenty-six wood cuts and two appendices. London and New York: Macmillan & Co., 1895. 697 pp. Price, five dollars.

When the original of this work on Theoretical Chemistry

[1] Ann. chim. phys. [3], **55**, 374 (1859).

from the stand-point of Avogadro's Law and Thermodynamics appeared about two years ago in Germany, it was immediately recognized that a growing demand had been met by Dr. Nernst. The comprehensive *Lehrbuch* of Ostwald, while serving as *the text* for the specialist in physical chemistry, was too exhaustive for the average reader in this line. On the other hand, the *Grundriss*, by the same author, was too brief for those who wished to advance beyond the mere elements of the subject. The book in question, occupies a position intermediate between the two above mentioned, and serves as a guide through what may be termed the second stages of physicochemical study. In dealing with the subject from the standpoint of thermodynamics, the author brings out the important bearing of the study of energy transformations on physicochemical problems. An idea of the contents of this volume can be gained best by glancing at the subjects treated. Book I deals with the gaseous, liquid, and solid states of matter, with physical mixtures, and dilute solutions. Book II has to do chiefly with the atomic theory, the kinetic theory of the molecule, determination of molecular weights, the constitution of the molecule, physical properties and molecular structure, dissociation of gases, and electrolytic dissociation. Book III treats of the law of chemical mass-action, chemical statics, homogeneous and heterogeneous systems, chemical equilibrium in salt solutions, and chemical kinetics; while Book IV discusses thermochemistry, electrochemistry, and photochemistry. Two appendices are added in the translation, the first giving a brief account of the work done in physical chemistry during the year 1893, and the second is a table of chemical periodicals.

The growing interest in physical chemistry in America and England seems to demand the translation of such a work, and a translation has been furnished by Dr. Palmer. The reviewer regrets that a comparison of the translation with the original necessitates not a little adverse criticism of the work of the translator. The attempt "to combine fidelity to the original, with clearness in good English," if successful in reference to the former, leaves much to be desired in respect to the latter. Examples are only too numerous. On page 311, we find that "chemically equivalent quantities of the most *various* (verschiedene) ions are set free from the *most various* (verschiedenste) solutions;" on page 335, that an electrolyte is made up of "positive and negitive *ingredients*" (Bestandtheile); on page 471, that "the saponification velocity, under conditions which are similar in other respects, is *actually proportional with very close approximation to*" (dass mit grosser Annäherung thatsächlich unter sonst gleichen Umständen die

Verseifungsgeschwindigkeit * * * proportional ist); on page 406 that "the relative depression of the vapor pressure, which is experienced by the solvent on adding a *strange* (fremde) substance;" on page 319 that "we may calculate *quite certainly* (sicher) the limiting value;" while on page 330 that "Arrhenius must be regarded as the *particular* (eigentlicher) father" of the dissociation theory, and the list could be extended much further.

Although the translation as a whole is unusually literal, yet erroneous translations are not wanting. On page 10 of the original we read, "Aeussere Arbeit, sowie kinetische Energie, bewegter Massen lässt sich auf mannigfache Weise und vollständig in einander überführen, sowie in Wärme verwandeln." In the translation, page 9, "external work," such as the kinetic energy of moving bodies may be transferred in many ways and completely into another form, as also into heat. On page 595 "Flüssigkeitsketten" is translated "liquid circuits," when liquid elements would have been less ambiguous. On page 648 it is stated that "Ramsay and Shields *insist*, *etc.*," while in the German we find "festsetzen." In many places, especially in the latter part of the book, the German word is given together with the English, indicating doubt in the mind of the translator, and in some cases such doubts could have been easily cleared up. Would it not have been better to give the nearest English equivalent, rather than fill the text with German words, since the translation is evidently for English readers?

It must, however, be remembered that it is no easy task to translate a book of this character, involving so many sides of physical chemistry, and written in a style which, though clear, is far from simple. The reader of this translation, who will overlook its shortcomings, will be able to obtain in most places a fair conception of what was meant by the author.

HARRY C. JONES.

ELEMENTARY QUALITATIVE CHEMICAL ANALYSIS, adapted for use in the Laboratories of Schools and Colleges. By FRANK CLOWES, D. Sc., (London), Professor of Chemistry in the University College, Nottingham, etc., and J. BERNARD COLEMAN, Senior Demonstrator of Chemistry in the University College, Nottingham, etc. Philadelphia: P. Blakiston, Son & Co., 1895.

Eleven pages of this book are devoted to use of apparatus, twenty to preparation and properties of oxygen, hydrogen, nitrogen, carbon dioxide, ammonia, chlorine, hydrochloric acid, distilled water, and nitric acid. The remaining 139 papes are devoted to qualitative analysis with free use of tables. The book seems neither better nor worse than dozens of others on

the same subject. Symbols are used everywhere instead of names. Prof. Clowes thinks this helpful to the student. It certainly is not agreeable to the average chemist to read a sentence like the following: "The solubility of $PbSO_4$ in $H\bar{A}$ and excess of AmHO," or like this; "Mix some powdered $Pb\bar{A}_2 . 3H_2O$ with about twice as much Na_2CO_3 in a cavity on a piece of charcoal." This book may, as Prof. Clowes thinks, supply a need in England, but why it should be republished in America is hard to understand, though only part of the great puzzle, Who uses the text-books on elementary qualitative analysis? A dozen new ones at least appear yearly, beside new editions of the old standards, and still new ones are written, differing in no marked way from the old, and—they find publishers. E. R.

ANLEITUNG ZUR DARSTELLUNG CHEMISCHER ANORGANISCHER PRÄPARATE FÜR CHEMIKER UND PHARMAZEVTEN. VON DR. REINHART BLOCHMANN, Professor an der Universitat Königsberg. Mit Abbildungen. Leipzig: Veit & Co., 1895.

This little volume gives minute directions for making 25 preparations. Dr. Blochmann has chosen preparations in which the raw materials are inexpensive, or are the products of preceding experiments. The length of time required, and variety in methods of work and forms of apparatus are also considered. The book can be recommended as clear, suggestive, and brief. E. R.

QUALITATIVE CHEMICAL ANALYSIS OF INORGANIC SUBSTANCES AS PRACTICED IN GEORGETOWN COLLEGE, D. C. New York: American Book Co., 1894.

This is a book of tables for elementary qualitative analysis, differing in some respects from those already in existence, but presenting no novel features calling for special notice.

E. R.